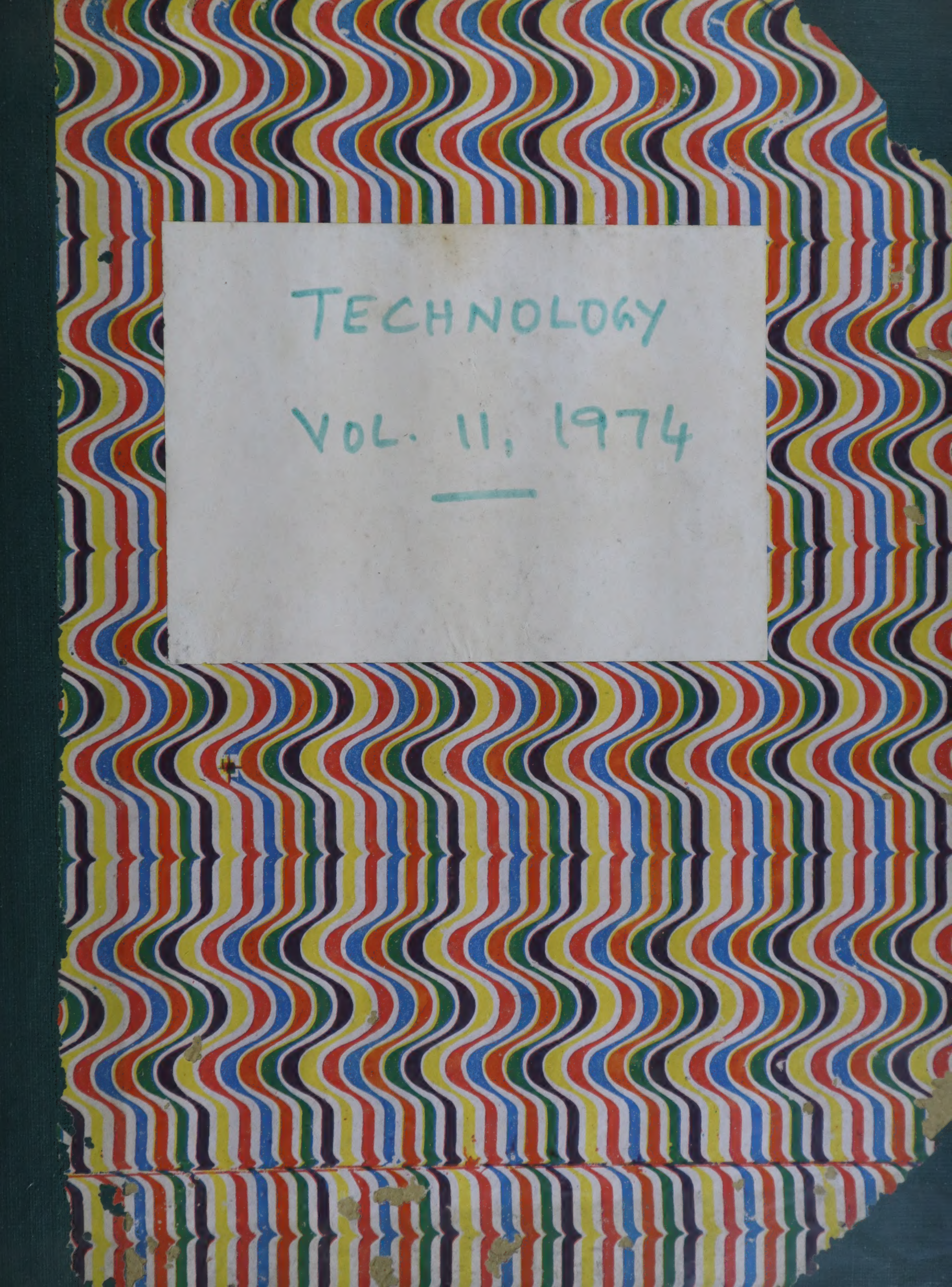




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UDC by K. M. SINHA, Asst. Librarian

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the views of the Planning and Development Division of the Fertilizer Corporation
of India Ltd.

Performances of three commercially available supported nickel catalysts, including one each of primary, secondary and single step autothermal reformation catalysts, have been studied. Experiments have been carried out at different temperatures within the range 700 to 850°C with a fixed methane concentration in the feed gas and also with different methane concentration varying between 0.06 and 0.14 mole fractions keeping the temperature fixed at 800°C. In all the experiments, the steam-to-carbon ratio (moles/atom) in the feed and the space velocity on the basis of the wet feed gas were maintained fixed at 4.0 and 10,000 respectively. The results indicate that the secondary reformation catalyst possesses maximum activity at all temperatures although at higher temperatures all the three catalysts show comparatively closer activity. While decrease in methane concentration in the feed results in a better approach to equilibrium with all the three catalysts, this effect is more pronounced in the case of the secondary and single step autothermal reformation catalysts than with the primary catalyst. It appears that the use of different catalysts, having specific properties to meet the different service conditions of primary, secondary and single step autothermal reformation, is of advantage.

Catalytic Methane-Steam Reformation—Effect of Temperature and Partial Pressure of Methane

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Catalytic steam-methane reformation has been studied by many workers and numerous patents for catalysts suitable for such a process are available. The present authors in their previous communications^{1, 2} have reviewed some of the important works on this subject.

Catalytic methane-steam reformation is a widely adopted process for the manufacture of hydrogen. Modern technology for the production of ammonia synthesis gas involves two-step reformation of natural gas, viz. primary and secondary reformation. In the primary step of reformation, major portion of the feed hydrocarbon is reformed with steam in presence of a catalyst in the temperature range 700 to 800°C producing a gas containing 6-10 per cent methane. In the secondary step, the effluent gas from primary reformation is equilibrated upto 1000°C in presence of steam and air so as to obtain a gas with negligible methane content. Air supplies oxygen to maintain high temperature in the secondary reformation and also provides nitrogen required in the synthesis gas.

Both primary and secondary reformation involve reaction between methane and steam but under differ-

ent service conditions. Primary reformation is an endothermic process requiring external source of heat and takes place at a comparatively lower temperature and higher concentrations of methane. The secondary reformation, on the other hand, is an autothermal process taking place in presence of both steam and air at relatively higher temperatures and lower partial pressures of methane.

Sometimes, a single step autothermal reformation process is adopted where methane-rich gas along with oxygen and steam is introduced into a reformer packed with catalyst.

Such differences in operating conditions of various reformation processes may require specific catalysts for specific condition. In fact, most of the catalyst manufacturers recommend separate catalysts for primary and secondary steps of reformation. But data supporting this view are not available in the literature. The present authors, in a previous investigation², studied both methane-steam and methane-steam-oxygen reactions in presence of some standard primary and secondary reformation catalysts. Under the experimental conditions adopted in that investigation

none of the catalysts showed any specificity towards any of the two processes.

Since primary and secondary reformation process differ mainly with respect to operating temperature and partial pressure of methane the present investigation includes studies on the performance of some standard catalysts under varying conditions of temperature and partial pressure of methane.

Experimental

Three commercially available supported nickel catalysts, designated as A, B and C, have been chosen for the present investigation. Catalyst A is in commercial use for primary reformation of natural gas, catalyst B has been widely used in secondary reformation process while C has been used in the single step autothermal reformation of methane-rich gas. The details of the catalysts including their BET surface area in the unreduced condition are given in Table 1.

TABLE 1—CHEMICAL COMPOSITION AND SURFACE AREA

Chemical Composition, % by wt.	Catalyst Sample		
	A	B	C
L.O.I. (at 900°C)	— 2.6	1.4	2.0
Al ₂ O ₃	— 75.4	86.9	90.2
NiO	— 15.3	11.8	6.8
CaO	— 6.1	—	—
CeO ₂	— 0.5	—	—
SiO ₂	— 0.05	0.12	0.14
Fe ₂ O ₃	0.03	0.05	0.03
Na ₂ O	0.02	0.01	0.01
Specific Surface Area, m ² /g.	39.7	51.2	46.4

The activity tests with these three catalysts were carried out in a bench scale unit similar to the one described earlier¹. A provision was made in the testing unit to feed a measured quantity of nitrogen to the steam-gas mixture entering the preheater in order to regulate the calculated partial pressure of methane in the feed stream. The feed gas used for the experiments, was the hydrocarbon fraction of coke oven gas containing 67-69 per cent methane, 6-8 per cent unsaturates, 9-13 per cent carbon monoxide, 1-3 per cent hydrogen and 9-13 per cent nitrogen. 30 c.c. of catalyst sized to 2 to 3 mm. grits, was charged in the reactor. The procedure followed for reduction of the catalysts was the same as described earlier². All the three catalysts were tested for their activity with respect to methane-steam reaction under atmospheric pressure maintaining preheat temperature at 600°C,

space velocity on the basis of total feed stream entering the reactor at 10,000 (c.c./c.c. of cat. hr⁻¹) and steam-to-feed carbon ratio at 4.0 (moles/atom).

Altogether, two series of experiments were carried out with each catalyst sample. In the first series, the reaction temperature was varied between 700 and 850°C and the concentration of methane was kept constant in the feed. In the second, partial pressure of methane in the feed was varied keeping the temperature fixed at 800°C. For varying the methane concentration in the feed without altering the space velocity, measured quantities of nitrogen were introduced along with the feed stream. Hydrocarbon gas, nitrogen and steam flows were so adjusted that the space velocity on the basis of total feed stream could be maintained at 10,000 hr⁻¹ keeping steam-to-carbon ratio fixed at 4.0. After completion of a series of experiment with each catalyst, its activity was checked under initial condition of experiment. No appreciable change in activity was observed during the period of experiments. Fresh catalyst was charged in each case for the second series of experiments.

Results and Discussion

The chemical composition and surface area of the three catalyst samples under investigation are given in Table 1. Essentially all the three were alumina-supported nickel catalysts. However, the primary reformation catalyst A contained, in addition to alumina and nickel oxide, components like calcia and ceria, which are believed to be responsible for arresting carbon laydown on the catalyst, a common feature particularly in primary reformation process. Catalyst B contained somewhat less nickel than A and did not have any other major component except traces of certain oxides present as impurities. Catalyst C is similar to B in chemical composition except that it contains much less nickel. It is reported that lower nickel content of an alumina-based catalyst makes it more resistant to thermal sintering³, and probably this lower nickel contents in catalysts B and C are desirable since they are required to work at much higher temperatures where loss of surface due to sintering at higher concentrations of nickel may be appreciable.

The surface area of the catalyst did not have any relationship with the nickel content. Catalyst B, having nickel content in between those of A and C, had the maximum surface area, whereas catalyst A, having the maximum nickel content, possesses minimum surface area. This is not unusual because surface area

depends not only on composition but also on method of preparation.

Variation of Temperature : The results of the series of experiments carried out under reaction temperatures varying from 700 to 850°C, are given in Table 2. This table gives the analysis of the feed and reformed gas on dry basis at various temperatures. Fig. 1 shows the variation of methane content of the reformed gas (on dry basis) with reaction temperature, whereas Fig. 2 shows the relationship between percentage equilibrium reaction and temperature. It follows from Figs. 1 and 2 that catalyst B possessed the maximum conversion efficiency at any temperature within the

range of experiment. The activities of the catalysts appeared to be somewhat proportional to their surface areas in the lower temperature region (below 800°C) as can be observed in Table 1 and Figs 1 and 2. However, such a relationship did not exist at higher temperature of reaction. Increase in conversion efficiency with temperature is sharper in case of catalysts A and C compared to what is observed in B so that at higher temperatures all the three catalysts have comparatively closer conversion efficiency.

Fig. 1 can be utilized for selection of a catalyst as well as operating temperature for any specific reformed gas composition. As for example, if 10 per

TABLE 2—VARIATON OF REACTION TEMPERATURES

[Space velocity—(wet gas) 10,000 c.c./c.c. of cat. hr⁻¹; Steam-to-carbon ratio (Moles/atom) 4.0; Preheat temperature—600°C]

Catalyst Sample	Volume and Wt. of Catalyst Charged	Reaction Temp., °C		Gas Composition, % by vol. (dry basis)						
				CO ₂	O ₂	Cn Hm	CO	H ₂	CH ₄	N ₂
A	30 c.c. (39.15 g.)	850	Inlet	—	0.6	7.2	9.8	2.0	68.0	12.4
			Outlet	8.2	—	—	16.4	68.2	3.6	3.6
		800	Inlet	—	0.6	6.8	9.6	2.8	67.0	13.2
			Outlet	10.8	—	—	10.0	59.2	15.0	5.0
		750	Inlet	—	1.0	7.0	12.0	2.6	67.2	10.2
			Outlet	11.6	—	—	8.2	46.0	29.0	5.2
		700	Inlet	—	1.0	7.0	12.0	2.6	67.2	10.2
			Outlet	10.4	—	—	9.0	34.0	39.4	7.2
B	30 c.c. (32.97 g.)	850	Inlet	—	1.0	6.8	13.2	1.0	68.6	9.4
			Outlet	9.4	—	—	16.4	69.4	2.2	2.6
		800	Inlet	—	1.0	6.8	13.2	1.0	68.6	9.4
			Outlet	11.8	—	—	12.6	64.0	8.4	3.2
		750	Inlet	—	0.8	7.2	9.6	2.6	67.0	12.8
			Outlet	11.0	—	—	10.0	58.2	15.8	5.0
		700	Inlet	—	0.8	7.2	9.6	2.6	67.0	12.8
			Outlet	12.0	—	—	8.0	56.0	18.4	5.6
C	30 c.c. (36.01 g.)	850	Inlet	—	1.0	6.6	9.8	2.2	68.2	12.2
			Outlet	8.8	—	—	15.6	65.8	6.0	3.8
		800	Inlet	—	0.8	8.2	10.4	1.2	68.8	10.6
			Outlet	10.2	—	—	12.2	59.0	14.6	4.0
		750	Inlet	—	0.6	7.4	11.0	1.8	68.6	10.6
			Outlet	11.2	—	—	10.0	46.8	27.0	5.0
		700	Inlet	—	0.8	7.0	12.4	2.0	68.0	9.8
			Outlet	11.0	—	—	10.0	39.6	33.8	5.6

cent is the upper limit of methane content of the reformed gas and if the temperature can be maintained at 850°C, any of the three catalysts is suitable. But if 800°C is the maximum allowable temperature, only catalyst B will be the choice for keeping the methane content of the reformed gas below 10 per cent. Conversely, if at 800°C a reformed gas containing more than 10 per cent methane is the requirement catalysts A and C will be preferred over catalyst B.

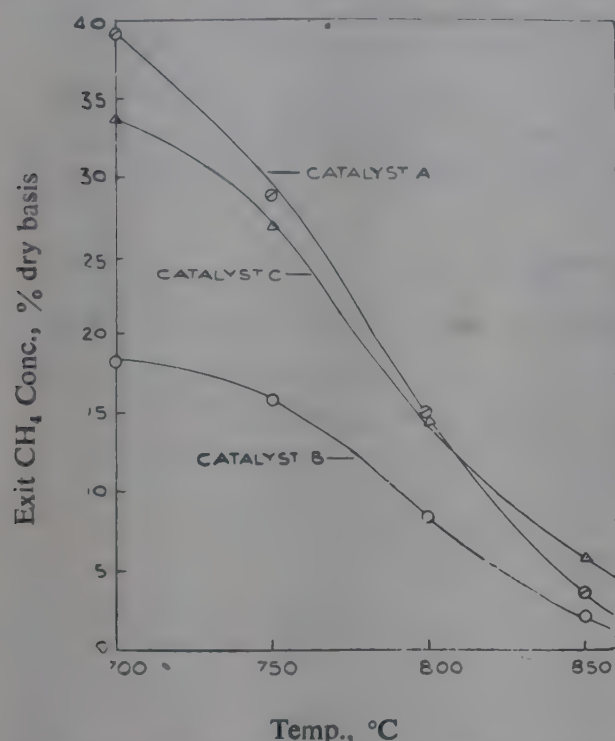


Fig. 1—Effect of Temperature on Methane Leakage

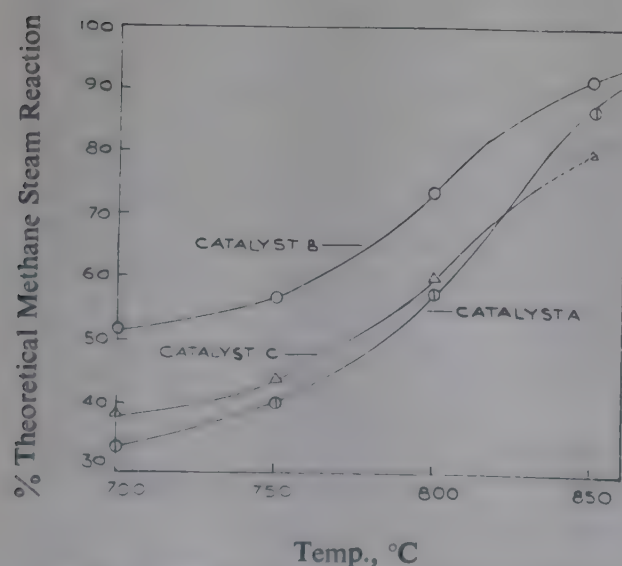


Fig. 2—Effect of Temperature on Approach to Equilibrium

It has already been mentioned that a secondary reformer runs at a considerably higher temperature to bring down the residual methane concentration to the lowest economic limit. This also requires a catalyst which can give very close approach to equi-

librium. Fig. 2 shows that closest approach to equilibrium can be achieved with catalyst B which, therefore, should be the choice for secondary reformation service.

The primary reformer exit gas, on the other hand, should contain an appreciable amount of methane to take part in secondary reformation so that a less active catalyst will be suitable for primary reformation process. Again, carbon liberation on the catalyst is a common problem in a primary reformer, particularly in the inlet side where the conditions, like high concentration of hydrocarbon and lower temperature, are favourable for carbon laydown. So, the primary reformation catalyst must have good selectivity to check carbon laydown. Very often higher activity of a catalyst is associated with poor selectivity. In fact, it has been reported that carbon liberation on a nickel catalyst tends to increase with increasing reforming activity of the catalyst⁴. So, the use of a less active catalyst in primary reformer is of advantage also to arrest carbon liberation. Catalyst A with much less reforming activity should, therefore, be preferred for primary reformation service. However, to improve the performance of a primary reformer and the life of the catalyst, the use of a composite catalyst bed consisting of a less active and more selective catalyst at the inlet side and a comparatively more active catalyst at the outlet side is often suggested.

The rates of methane-steam reaction in terms of moles of methane reformed per second per gram of catalyst have been calculated from the results of Table 2. Log values of the calculated rates $\left(-\frac{dx}{dt}\right)$ have been plotted against reciprocal of corresponding temperature expressed in degree Kelvin in Fig. 3. The activation energies for the three catalysts have been calculated from the slopes according to Arrhenius expression. The activation energies for catalysts A, B and C are 33.4, 15.5 and 27.4 Kcals/mole respectively. It is evident from the results that catalyst B has got much higher intrinsic activity compared to the other two catalysts.

Variation of Partial Pressure of Methane in the Feed: The results of the experiments carried out with varying initial concentration of methane are shown in Table 3. The effect of variation of initial methane concentration on the residual methane content of the reformed gas and percentage equilibrium reaction are illustrated in Figs. 4 and 5 respectively.

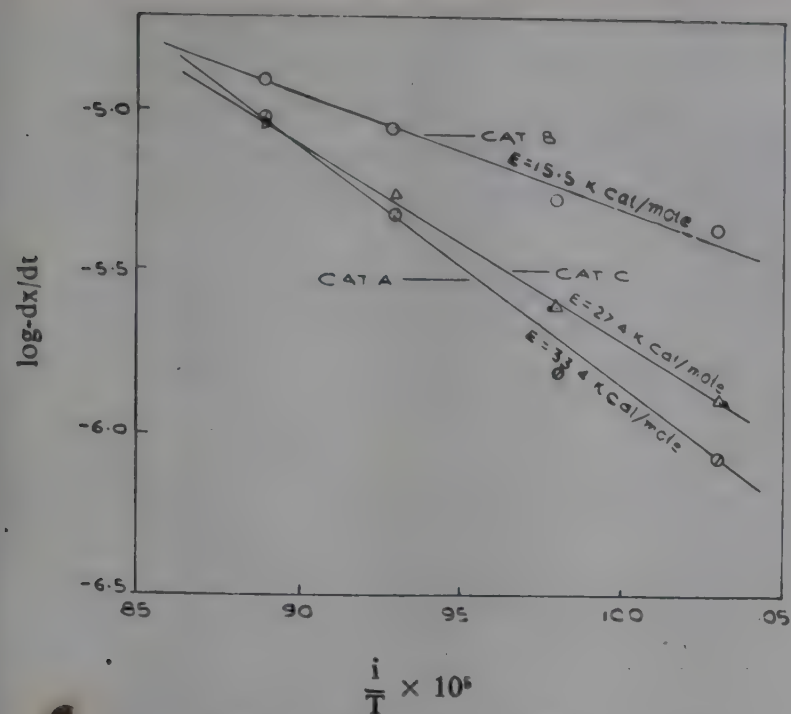


Fig. 3—Effect of Temperature on Reaction Rate

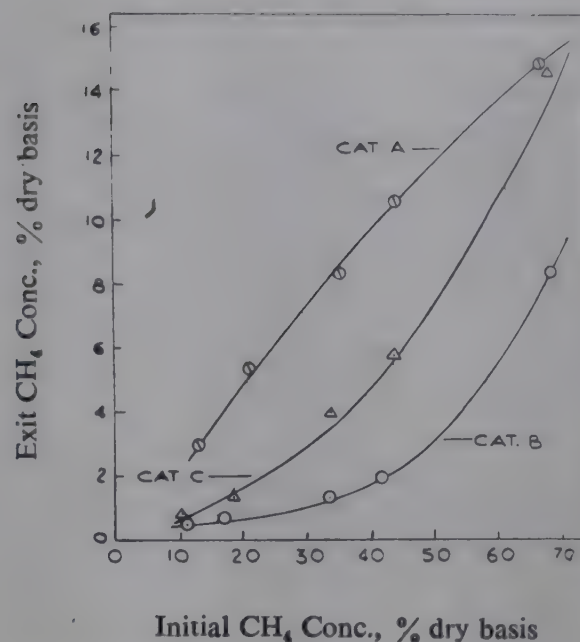


Fig. 4—Effect of initial Methane Concentration on Methane Leakage

TABLE 3—VARIATION OF INITIAL METHANE CONCENTRATION

[Space velocity—10,000 c.c./c.c. of cat. hr⁻¹; Steam to-carbon ratio (moles/atom) 4.0; Preheat temperature 600°C; Reaction temperature—800°C]

Catalyst Sample	Volume of Catalyst Charged, c.c.		Gas Composition, % by vol. (dry basis)						
			CO ₂	O ₂	Cn Hm	CO	H ₂	CH ₄	N ₂
A	30	Inlet	—	0.6	6.8	9.6	2.8	67.0	13.2
		Outlet	10.8	—	—	10.0	59.2	15.0	5.0
		Inlet	—	0.4	4.2	7.2	2.4	44.2	41.6
		Outlet	9.0	—	—	10.0	50.6	10.6	19.8
		Inlet	—	0.4	3.0	6.0	2.0	35.4	53.2
		Outlet	9.0	—	—	8.4	46.8	8.4	27.4
		Inlet	—	0.2	1.0	4.2	1.4	21.2	72.0
		Outlet	6.6	—	—	6.4	34.6	5.4	47.0
		Inlet	—	0.2	0.4	2.2	0.4	13.0	83.8
		Outlet	4.0	—	—	5.2	25.2	3.0	62.6
B	30	Inlet	—	1.0	6.8	13.2	1.0	68.6	19.4
		Outlet	11.8	—	—	12.6	64.0	8.4	3.2
		Inlet	—	0.6	4.6	7.8	2.6	41.4	43.0
		Outlet	10.6	—	—	10.4	61.4	2.0	15.6
		Inlet	—	0.4	4.0	6.6	1.8	33.2	54.0
		Outlet	9.6	—	—	9.4	56.4	1.4	23.2
		Inlet	—	0.2	2.2	2.4	0.6	16.6	78.0
		Outlet	6.4	—	—	7.2	40.2	0.8	45.4
		Inlet	—	0.2	1.0	2.0	0.2	10.8	85.8
		Outlet	4.6	—	—	5.8	29.2	0.6	59.8
C	30	Inlet	—	0.8	8.2	10.4	1.2	68.8	10.6
		Outlet	10.2	—	—	12.2	59.0	14.6	4.0
		Inlet	—	0.6	4.4	8.0	1.0	44.0	42.0
		Outlet	10.2	—	—	10.6	56.6	5.8	16.8
		Inlet	—	0.4	3.2	6.0	0.4	34.2	55.8
		Outlet	9.2	—	—	9.6	51.6	4.0	25.6
		Inlet	—	0.2	1.8	3.2	0.4	18.6	75.8
		Outlet	6.8	—	—	7.6	40.2	1.4	44.0
		Inlet	—	0.2	1.2	2.0	0.2	10.6	85.8
		Outlet	4.2	—	—	6.0	29.6	0.8	59.4

Fig. 4 shows that irrespective of methane concentration in the feed gas catalyst B gives lowest methane slip in the reformed gas and catalyst A gives highest. This also shows the higher activity of Catalyst B.

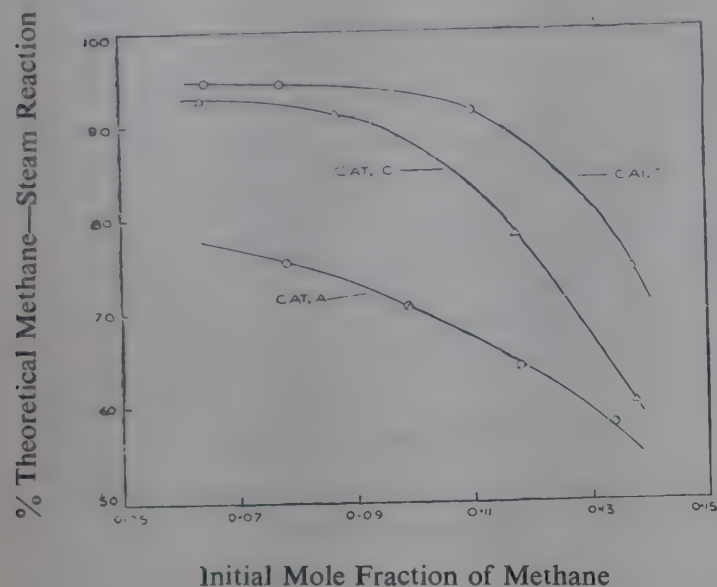


Fig. 5—Effect of Initial Methane Concentration on Approach to Equilibrium

It is observed from Fig. 5 that percentage equilibrium conversion is inversely related to initial methane concentration. But it is interesting to note that the effect of decreasing concentration of methane in the feed on the percentage equilibrium conversion, is considerably more in case of catalysts B and C than what is observed in case of catalyst A. So, it follows that efficiency of catalysts B and C relative to that of catalyst A increases at lower initial concentrations of methane. This again clearly demonstrates the advantage of using catalyst B in secondary

reformation where initial methane concentration is much less and where closer approach to equilibrium is always desirable to maintain low inert level in the ammonia synthesis gas. Closer approach to equilibrium is also desirable in single step autothermal process.

Summarizing the results and observations it is reasonable to conclude that the use of different catalysts in primary, secondary and autothermal reformation processes having specific properties to meet the demands of desired service conditions, is necessary. While primary reformation requires a catalyst having lower intrinsic activity but more selective towards prevention of carbon liberation, a secondary reformation catalyst is required to have high intrinsic activity and high resistance to thermal sintering. Service conditions of single step auto-thermal reformation are similar to those of secondary reformation excepting that methane concentration in the feed is high and a catalyst similar to secondary reformation catalyst appears to be suitable.

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[Original mss. received on Aug. 14, 1972]

The thermal decomposition characteristics of nickel dimethylglyoxime were investigated by the TGA, DTA and magnetic measurements. Nickel dimethylglyoxime decomposes in air or nitrogen atmosphere probably to form NiN_2 at 287°C . This compound has a high specific magnetic susceptibility but it is antiferromagnetic in nature, which has been characterized by a sharp Neel temperature at 265°C . It decomposes in air at 325°C to form nickel and some nickel oxide. While in the nitrogen atmosphere, another compound, probably NiN , is formed at 440°C . This compound is ferromagnetic in nature without having a sharp Curie point. In air, it decomposes at 310°C to form metallic nickel along with some nickel oxide.

Thermal and Magnetic Studies on the Decomposition of Nickel Dimethylglyoxime

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Introduction

Nickel dimethylglyoxime is a well-known complex compound, widely used to estimate nickel, because of the sensitivity of the reaction and stability of the complex. Although its thermal characteristics have been studied^{1,2} in the early days of its discovery, a detailed investigation on the thermal stability and decomposition characteristics has not been made. In this report, an attempt has been made to interpret the decomposition characteristics and to analyse the decomposition products formed in an oxygen-rich and an inert atmospheres. The TGA and DTA thermograms have been discussed and the results correlated with the magnetic properties.

Experimental

Preparation of the Sample : The complex compound was precipitated by a saturated ethanolic solution of dimethylglyoxime from a 10 per cent (w/v) A.R. nickel nitrate solution at 60°C . The precipitate was thoroughly washed with ethanol solution to make it free of the precipitant. The precipitate was then dried in an air oven at 110°C for 6 hours and kept in a stoppered polythene bottle.

Thermogravimetric Analysis : A precision quartz spring balance enclosed in an all-glass housing was used for the thermogravimetric analysis. The change in weight was observed from the vertical displace-

ment of an indicator by a micrometer microscope. A weighed amount of the sample was taken in a glass bucket and the temperature of the sample was raised at the rate of $5^\circ\text{C}/\text{min}$. by a manually operated auto-transformer, which powered a non-inductive nichrome wire heater wound over the sample jacket. The sensitivity of the balance was 0.0148 mg.

Differential Thermal Analysis : The dual-cell DTA unit used in the present study has been described elsewhere³. A specially designed all-glass attachment was used with the furnace for DTA runs in an inert atmosphere. The furnace was heated by a manually operated auto-transformer. The thermograms were recorded by programming the temperature at the rate of $5^\circ\text{C}/\text{min}$.

Magnetic Measurements : A Faraday-type magnetic balance was used for the magnetic measurements. This accessory was a part of the TGA unit already described. Magnetic susceptibilities were measured under running vacua of the order 10^{-5} torr. The instrument was calibrated with A.R. ferrous ammonium sulphate. A weighed amount of a sample (1-5 mg.) was used for the thermomagnetic studies.

Results & Discussion

The TGA curve for nickel dimethylglyoxime in air is shown in Fig. 1A-I and the corresponding DTA thermogram in Fig. 1B. The TGA curve in air indi-

cates that the complex decomposes in two steps. Firstly, a slow loss in weight begins at 210°C until an abrupt sharp loss (62 per cent) is noticed at 287°C due to the decomposition of the complex. This is followed by another small loss in weight (31.5 per cent of the residue) at 325°C. The initial slow loss in weight (5 per cent) was found to be due to sublimation of the complex. The volatilized compound was deposited on the colder part of the sample jacket. It is known from the literature⁴ that nickel dimethylglyoxime volatilizes after 250°C. But Duval⁵ contradicted the sublimation of the complex, except in vacuum, and proposed a loss of four nitrosyl groups when decomposed in air. Thermomagnetic behaviour of the end-product obtained at 500°C from the TGA run in air was investigated. The curve I (Fig. 2) represents the specific susceptibility values against temperatures for this residue. The pattern corresponds to the thermomagnetic nature of the massive nickel particles with a distinct Curie temperature at 355°C. The ferromagnetic particles from the residue were later separated by a horse-shoe magnet and the remaining black powder was heated in air for some time at 500°C to oxidize any carbon or ferromagnetic particle which might be present in the residue. There was no loss in weight and the specific susceptibility of the residue at 25°C was found to be 46.33×10^{-6} c.g.s. units corresponding to that of the nickel oxide.

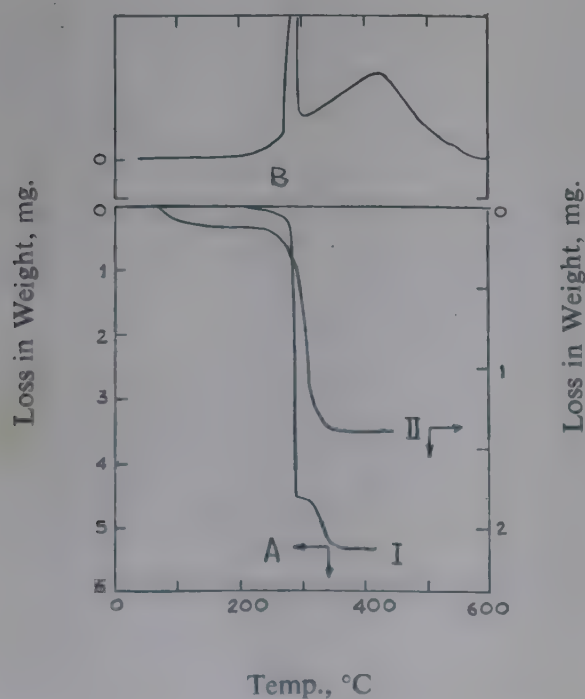


Fig. 1

A: TGA thermograms in air of 7.1 mg. nickel dimethylglyoxime (Curve-I) and 7.3 mg. decomposition product (500°C) of the complex compound (Curve-II) in nitrogen atmosphere.
B: DTA thermogram of the complex compound in air.

This indicates that nickel dimethylglyoxime when decomposes in air at 500°C gives massive nickel particles along with some nickel oxide. Duval⁵ found carbon and metallic nickel in the air-decomposed product. The material balance from the TGA thermogram gives a probable scheme of decomposition of the complex compound. The sharp loss in weight (62.0 per cent) might be due to the simultaneous rupture of the two dimethylglyoxime rings to give an intermediate compound NiN_2 , which breaks at 325°C in air to form metallic nickel particles. The smaller nickel particles are oxidized in air to form nickel oxide.

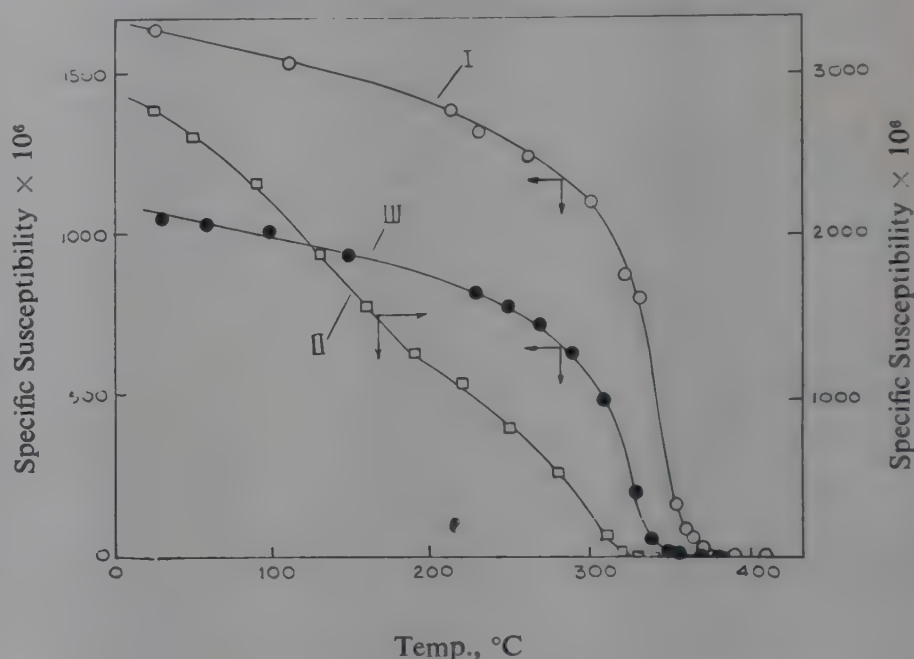


Fig. 2—Thermomagnetic behaviours of the decomposition products (500 °C) in air (Curve I) and nitrogen (Curve II) atmosphere of nickel dimethylglyoxime Curve III represents the decomposition products of NiN in air.

The DTA curve (Fig. 1B) of the precipitate in air shows that both the reactions are exothermic as indicated by the two exothermic peaks. At 287°C, the rupture of the two rings causes evolution of heat, so that the temperature in the sample momentarily shoots up to 600°C, which was measured by parallel experiments. The sharp exothermic peak is followed by an exothermic hump. A number of parallel experiments showed that these slow exothermic humps have no definite peak temperature. This hump is due to the aerial oxidation of finely divided nickel particles. This was confirmed by conducting the same experiment in an inert atmosphere of nitrogen. Thus, the DTA thermogram of nickel dimethylglyoxime in air supports the decomposition of the complex at 287°C but the two steps degradation which was observed in the thermogravimetric analysis (Fig. 1A-I) could not be detected.

The TGA and DTA thermograms of nickel dimethylglyoxime in nitrogen atmosphere are shown in Figs. 3A and 3B respectively. It may be observed from the TGA curve that the volatilization starts at 240°C and proceeds upto 287°C until the complex is decomposed. The material balance suggests that about 4.5 per cent sublimation of the complex is following by a sharp loss in weight corresponding to 61.5 per cent. This loss fits for the degradation of nickel dimethylglyoxime to form NiN_2 . A further loss in weight (16 per cent) was noticed at 440°C. It is, therefore, suspected that the intermediate product NiN_2 further breaks in a nitrogen atmosphere probably to form NiN . After the TGA run, the residue was evacuated to 10^{-5} torr and the thermomagnetic behaviour of the product was studied, which is shown in curve II (Fig. 2). The magnitudes of the specific susceptibility values suggest ferromagnetism in the specimen but the thermomagnetic behaviour is very different from that of the massive nickel particles. This suggests that the decomposition of nickel dimethylglyoxime in a nitrogen atmosphere produces a ferromagnetic nickel compound.

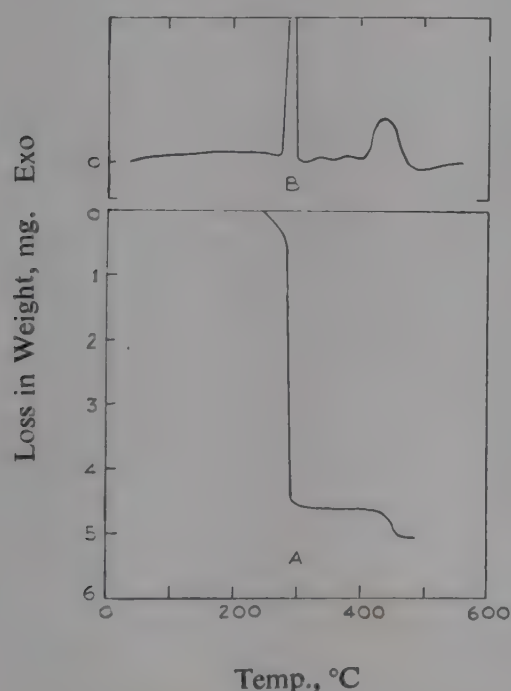


Fig. 3

A: TGA thermogram in nitrogen atmosphere of 7.5 mg. nickel dimethylglyoxime.

B: DTA thermogram of the complex compound in nitrogen atmosphere.

The DTA thermogram of the precipitate in nitrogen atmosphere (Fig. 3B) shows that the nickel complex breaks at 287°C giving a sharp exothermic peak as observed in air (Fig. 1B). But the absence of the slow exothermic hump in this case confirms the aerial oxidation of nickel observed in air after the decom-

position of the complex. A further minor exothermic decomposition was observed at 440°C. This corresponds to the small loss in weight (16 per cent) in the TGA run in the nitrogen atmosphere shown in Fig. 3A. The residue obtained at 500°C after the differential thermal analysis in nitrogen atmosphere was further studied. The thermal stability of this product in air was investigated by thermogravimetric analysis and the course of its decomposition is shown in Fig. 1A-II. The TGA thermogram shows a loss in weight corresponding to 19.12 per cent at 310°C. This loss quantitatively fits for the decomposition of NiN to form metallic nickel particles. The thermomagnetic behaviour of the end-product is given in Fig. 2-III. The curve shows a ferromagnetic nature which is similar to that of the massive nickel. The magnitudes of the specific susceptibilities indicate the presence of some nickel oxide also along with the metallic particles. It appears, therefore, that the decomposition of nickel dimethylglyoxime in nitrogen atmosphere occurs in two steps. Firstly, at 287°C where the complex breaks to form NiN_2 and then NiN is formed at 440°C. This residue (NiN) is stable in nitrogen atmosphere upto 500°C but decomposes in air at 310°C to form metallic nickel and nickel oxide.

The decomposition of nickel dimethylglyoxime in air or in nitrogen gives an intermediate nickel compound. The thermogravimetric data in both the cases corresponds to the molecular formula of the intermediate as NiN_2 . In air, this intermediate decomposition product is stable upto 325°C, while in the nitrogen atmosphere the stability extends to 440°C. To investigate the magnetic properties of the compound, a weighed amount of nickel dimethylglyoxime was decomposed in the nitrogen atmosphere at 287°C in the magnetic balance. The temperature was raised upto 320°C and then cooled down to room temperature. The sample was evacuated up to 10^{-5} torr and then magnetic measurements were made on the sample. The specific susceptibility vs temperature of this compound is shown in Fig. 4-1. The magnetic behaviour of this compound was found to be very peculiar. The specific susceptibility values showed that the compound is neither strongly ferromagnetic nor paramagnetic in nature. On the other hand, the material showed antiferromagnetism which was identified by a characteristic Néel temperature at 265°C. The observed susceptibility values after 300°C are joined to the main curve by a broken line, since a small loss in weight was noticed at 310°C showing that the NiN_2 decomposes in vacuum at this temperature. The mag-

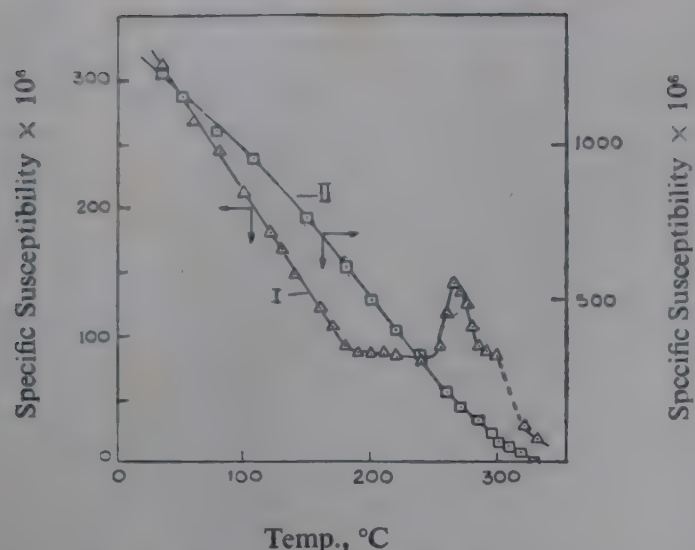


Fig. 4—Thermomagnetic behaviours of the first decomposition product of nickel dimethylglyoxime (Curve-I) in nitrogen atmosphere and after decomposition at 310°C intermediate product in vacuum (Curve-II)

netic susceptibility against temperature for the end-product obtained at 330°C is shown in Fig. 4-II. The thermomagnetic behaviour of the end-product is similar to NiN as shown in Fig. 2-II. However, the susceptibility values in this case were not so high. This might be due to the preparation of the sample at a relatively lower temperature.

Conclusion

Nickel dimethylglyoxime decomposes in air or nitrogen atmosphere at 287°C. The decomposition reactions are exothermic in nature. From the thermogravimetric data the molecular formula of the residue

was found to correspond to NiN₂. The thermomagnetic behaviour of this compound is very peculiar; its anti-ferromagnetism is characterized by a sharp Néel temperature at 265°C. Further, this intermediate compound decomposes in air at 325°C, to form metallic nickel along with some nickel oxide, which were identified from magnetic data. However, in the nitrogen atmosphere, a loss in weight and an exothermic change were noticed at 440°C. The decomposition product obtained upto 500°C shows ferromagnetism without a sharp Curie point. It decomposes in air at 310°C and the material balance from the TGA data corresponds to the molecular formula as NiN. The decomposition product of NiN in air shows a mixed thermomagnetic behaviour of the metallic nickel and nickel oxide.

X-ray and other physico-chemical studies on the new compounds, viz. NiN and NiN₂, reported in this work will be communicated shortly in a separate paper.

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Four catalyst samples containing 12 per cent nickel oxide and different concentrations of lime and γ -alumina have been studied for hydrocarbon-steam reforming activity, resistance to carbon laydown, mechanical stability and specific surface area before and after reduction. The results show that the activity and specific surface area increase with increase of lime and γ -alumina upto a certain extent beyond which the trend is reversed. Resistance to both carbon laydown and dusting, however, increases with increases of lime and γ -alumina without any reversal of trend.

Role of Lime and Gamma - Alumina on the Activity, Selectivity and Mechanical Stability of Hydrocarbon-Steam Reforming Catalyst

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Supported nickel catalysts are widely adopted for the catalytic hydrocarbon steam-reforming processes. Although a nickel catalyst supported on pure alumina is highly active for the hydrocarbon-steam reforming process, it is poor in selectivity to resist carbon laydown and also does not possess sufficient mechanical stability. So, unless the structure and composition of the alumina supported nickel catalyst are suitably modified, such a catalyst will be totally unsuitable for commercial application. Numerous patents are available in the literature describing various formulations of supported nickel catalysts for hydrocarbon-steam reformation but only a few of them ¹⁻⁷ have been proved to be fool proof from the point of view of commercial application.

Some of the present authors have studied the effect of varying proportions of α - and γ -alumina in the carrier on the physical structure as well as activity, selectivity and mechanical stability of nickel catalysts^{8, 9}. Those studies reveal that while increasing concentration of γ -alumina has favourable effects on surface area, porosity, pore size distribution, mechanical strength and resistance to dusting of nickel catalyst with a fixed nickel content there is an optimum ratio of α - and γ -alumina which gives maximum activity. However, incorporation of γ -alumina favours carbon laydown on the catalyst probably due to increase of acid centres.

The favourable effects of alkali and alkaline-earth metal oxides in preventing carbon laydown on the nickel catalyst are well known¹⁰⁻¹⁴. So, the present authors in a previous investigation¹⁵ studied the effects of incorporating lime along with γ -alumina in the carrier of nickel catalysts in order to inhibit the carbon laydown. It has been observed that incorporation of lime and γ -alumina in the carrier of nickel catalyst to the extent adopted in that investigation¹⁵ improves not only activity, mechanical strength and resistance to dusting but also the resistance to carbon laydown on the catalyst.

However, in that investigation lime content was varied upto 16 per cent and coprecipitated alumina upto 12 per cent by weight. The present investigation studies further the role of lime and coprecipitated alumina (providing γ -alumina) maintaining a fixed molar ratio between them and varying their concentrations in a wider range. In fact, the lime content has been varied upto 30 per cent and coprecipitated alumina content has been adjusted to maintain a constant molar ratio of 1:1 with the lime content keeping the nickel oxide concentration fixed around 12 per cent by weight in the catalysts studied in this investigation. The studies comprise surface area, activity, resistance to carbon laydown and mechanical stability of four catalyst samples.

Experimental

Preparation of Catalyst : Altogether four samples of nickel catalysts were prepared by coprecipitation varying the ratio of precalcined alumina (α -alumina), lime and coprecipitated alumina which provides γ -alumina in such a manner that lime and coprecipitated alumina were always in the molar ratio. Finely powdered precalcined alumina was suspended in a solution containing nickel, aluminium and calcium nitrates and the requisite amount of ammonium carbonate solution was added for precipitation. The precipitated mass mixed up with precalcined alumina was then filtered, partially dried, formed into cylindrical tablets of 6 mm. $\times$ 6 mm. and finally cured at 650-700°C. The nickel oxide content in all the catalysts was maintained approximately same, around 12 per cent (Table 1).

Table 1—Composition of the Catalysts

Sample No.	Precalcined Al_2O_3 , %	Coprecipitated, %		NiO
		Al_2O_3	CaO	
CN 1	73.9	9.1	4.8	11.9
CN 2	59.8	18.2	9.6	12.1
CN 3	31.6	36.4	19.9	11.8
CN 4	3.4	54.6	29.6	12.0

Activity and Stability Tests : All the four catalyst samples were tested for activity and stability in a bench scale unit described elsewhere⁹. 25 g. of catalyst pellets were charged in the reactor in each case. Reduction of catalyst in the reactor was carried out with a mixture of steam and hydrogen containing 10 mole per cent of the latter at 700°C for a period of 8 hours. Pure *n*-heptane was used as feed hydrocarbon and steam to carbon ratio (moles H_2O /atom C) at the inlet was maintained fixed at 4.0. All the tests were carried out under atmospheric pressure and the heptane-steam mixture entering the catalyst bed was preheated to 500°C. During initial period of activity tests, the liquid hourly space velocity (LHSV) with respect to heptane was varied between 0.6 and 1.0 (c.c. of heptane/g. cat/hr) keeping the catalyst bed exit temperature fixed at 850°C. Then keeping the LHSV with respect to heptane fixed at 1.0 the catalyst bed exit temperature was varied between 850 and 700°C. Under each set of operating conditions after attaining steady state, outlet gas samples were collected after condensing the unreacted steam and analysed in an orsat apparatus to determine the composition

of the reformed gas on dry basis. The activity tests under various operating conditions, as mentioned above, were completed during a period of 25 hours. Each catalyst was then tested for a further period of 60 hours under a fixed operating condition of 1.0 LHSV and 750°C to assess stability. Finally, each catalyst was subjected to steaming at 850°C for 4 hours to remove carbon, if any, and then the reactor was cooled down in a nitrogen stream. The catalyst was discharged and weighed after removing adhered dust if any.

Specific Surface Area : Specific surface areas of the unreduced fresh catalyst samples as well as of the reduced samples after activity and stability tests were determined by nitrogen adsorption at liquid nitrogen temperature using BET equation.

Results and Discussion

X-ray Analysis : X-ray diffraction studies on the fresh catalyst samples revealed that the γ -alumina content increases with the increasing amount of coprecipitated alumina in a catalyst. Thus, the catalyst CN-1 with minimum amount of coprecipitated alumina shows least γ -alumina content whereas the catalyst CN-4 with maximum amount of coprecipitated alumina shows the highest γ -alumina content. However, this is only qualitative as quantitative estimation of α - and γ -alumina contents of the catalyst samples could not be carried out. X-ray studies also revealed that there is a tendency of increase in concentration of spinels, like nickel and calcium aluminates, in the catalysts with increase of lime and coprecipitated alumina contents.

Activity : The activities of catalysts have been computed in terms of percentage of input carbon reformed into carbon monoxide and dioxide. The activities at 850°C have been plotted against liquid hourly space velocity (LHSV) in Fig. 1 and similarly, activities at a constant LHSV of 1.0 have been plotted against reaction temperatures in Fig. 2. Within the range of experimental conditions adopted, the catalyst CN-3 corresponding to 20 per cent lime and 37 per cent coprecipitated alumina shows highest activity under all conditions of experiments. Thus, the composition of CN-3 appears to be optimum with respect to lime and γ -alumina contents. In a previous investigation⁹ while studying the effect of γ -alumina alone, the highest activity was observed with the catalyst prepared with about 40 per cent coprecipitated alumina. So, the present results showing that catalyst corresponding to 37 per cent coprecipitated alumina

content possesses maximum activity, more or less conform to the earlier observation.

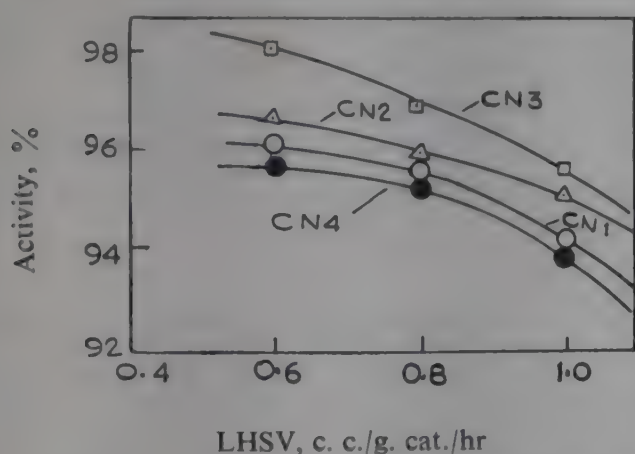


Fig. 1—Activity at Different Space Velocities

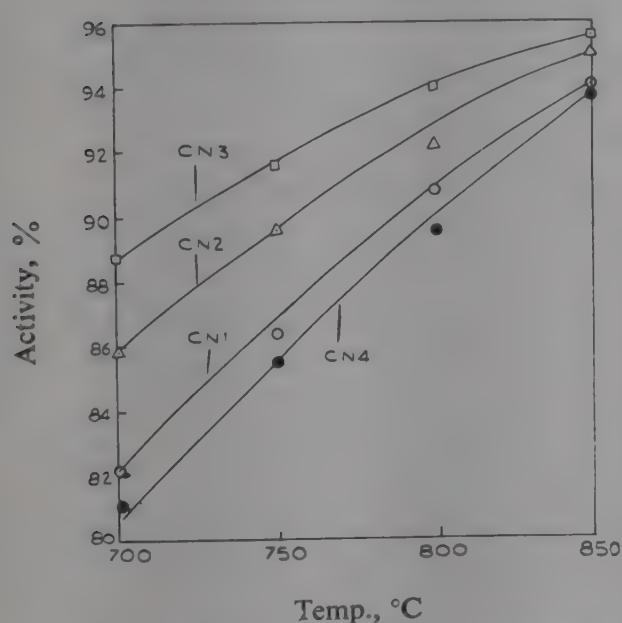


Fig. 2—Activity at Different Temperatures

Carbon Laydown: Carbon laydown on the catalyst has been computed in terms of per cent of input carbon from the carbon balance between feed and exit gases on hourly basis. This gives a fairly good comparative idea about carbon laydown on different catalysts. Percentage carbon deposited on catalyst under a fixed operating condition of 1.0 LHSV and 700°C has been plotted against corresponding lime content (Fig. 3). It is observed from this figure that carbon laydown on the catalyst decreases with the increase of lime content inspite of the fact that this is also accompanied by increase of γ -alumina which normally favours carbon laydown⁹. This appears to be due to the fact that the acceleration of carbon liberation due to γ -alumina in the catalysts is more than balanced by the inhibition of the same by lime content.

Mechanical Stability: Mechanical stability of a catalyst can be fairly assessed from its resistance to dust-

ing or erosion under actual service condition. Loss of catalyst due to erosion during initial activity tests as well as during the prolonged run of 60 hr. under a comparatively severe operating condition of 1.0 LHSV and 750°C has been estimated from the difference in weight of catalyst tablets charged and that of discharged catalyst tablets after removing the adhered dust, if any. The percentage loss of catalyst (by weight) due to dusting has been plotted against corresponding lime content (Fig. 4). It is observed that resistance to erosion of catalysts increases with increase in lime content which was observed in an earlier investigation¹⁵ also. This appears to be due to the fact that increase in lime and γ -alumina contents in the catalyst increases the formation of nickel and calcium aluminates spinels which are believed to improve mechanical stability¹⁶.

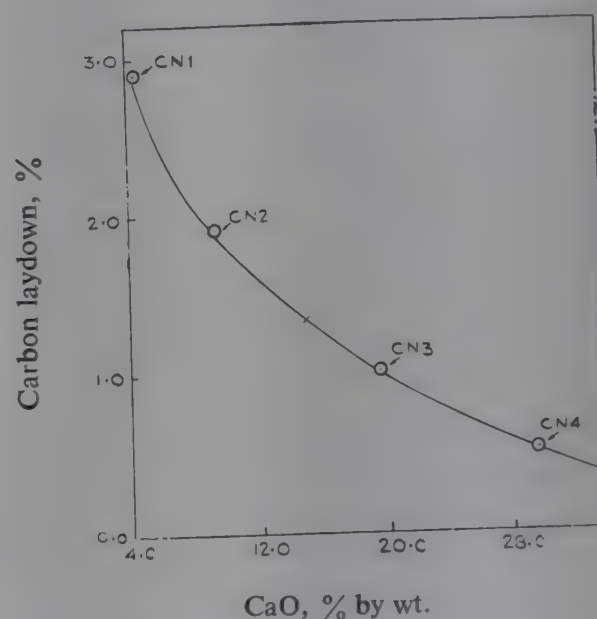


Fig. 3—Carbon Laydown on Catalysts

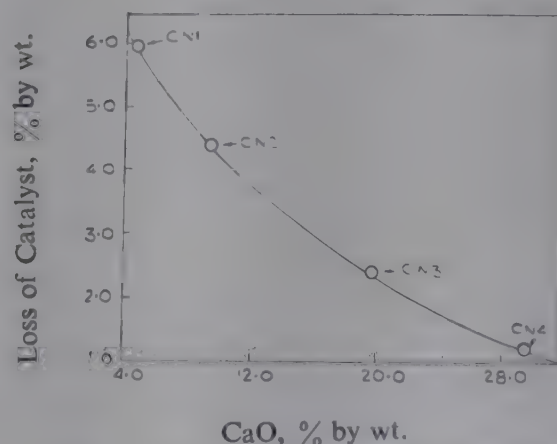


Fig. 4—Mechanical Stability of Catalysts

Specific Surface Area: The specific surface areas of both fresh and reduced catalyst samples have been plotted against lime contents (Fig. 5). There is a considerable shrinkage of surface area of the cata-

lysts after reduction and activity and stability tests. However, the relative positions of the catalysts with respect to surface area remain unchanged after reduction and tests. Fig. 5 shows that there is an optimum composition with respect to lime and γ -alumina contents (around that of CN-3) which gives the maximum surface area. The variation of surface area of the catalysts is similar to that of their activities. Thus, catalyst CN-3 having maximum surface area shows highest activity (Figs. 1 & 2). In earlier investigations^{8,9} it was observed that with increase of γ -alumina content the surface area continuously increases. But in the present case, since the increase in γ -alumina content is accompanied by corresponding increase of lime, the latter might have favoured sintering so that at higher concentrations of CaO the increase in surface area due to γ -alumina is more than balanced by reduction of surface due to sintering as is observed with the catalyst CN-4, giving an overall effect of lowering of surface area. Thus, the sintering effect of lime appears to be the cause of reversal of trend of surface area and activity of the catalysts.

The activities of the catalysts at 750°C as well as their specific activities (activity per unit area) have

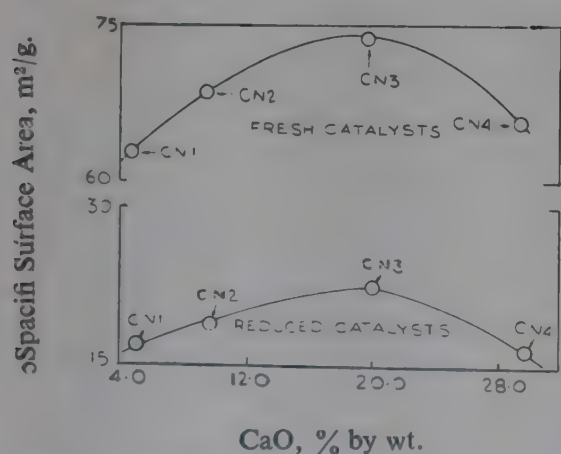


Fig. 5—Specific Surface Area of Fresh and Reduced Catalysts

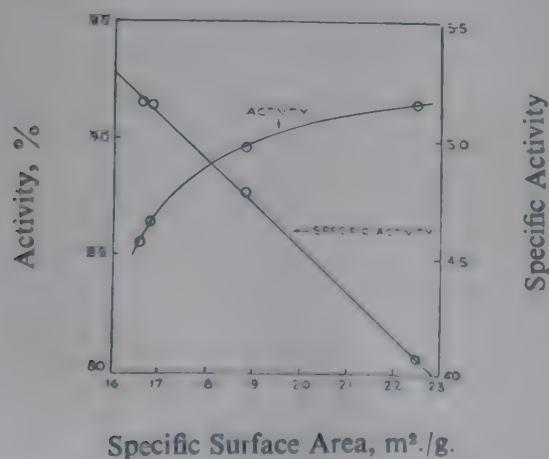


Fig. 6—Variation of Activity with Surface Area

been plotted against specific surface area of the reduced samples (Fig. 6). It follows from this figure that although the activity increases with increase of specific surface area, the variation is not exactly proportional to specific surface area (also shown in Fig. 6). This is apparently due to the fact that nickel concentration of the catalysts remaining fixed, concentration of active sites decreases with the increase of surface area.

Conclusion

It can be concluded from the observations made in the present investigation that with a fixed nickel content incorporation of lime alongwith γ -alumina in a reformation catalyst can improve its surface area and activity upto a certain optimum concentration beyond which the effect is reverse. However, mechanical stability and resistance to carbon laydown increase with increase of these constituents without any reversal of trend.

Acknowledgement

The authors acknowledge with thanks the service rendered by Dr. S. K. Ghosh and his co-workers of the Physical Research Wing in supplying information on X-ray diffraction analysis of the catalyst samples.

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Acidity and basicity of samples of alumina, silica and silica-alumina, calcined at different temperatures, have been measured by exchange with different electrolytes and by titration using Hammett indicators. The water vapour adsorption and acidity measurements have been carried out at different partial pressures of water vapours. In all the samples acidity/basicity have been found to increase up to the formation of monolayer and beyond that a process of regular decrease and increase set in. This has been explained by assuming coverage of acid/base sites by physisorbed water and aggregation of physisorbed water molecules resulting in exposure of original surface sites.

Relationship between Water Adsorption and Acidity Over Alumina, Silica and Silica-Alumina Catalyst

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Introduction

The acidic properties of silica, alumina and silica-alumina make them useful catalysts for reactions, like cracking, isomerization, reforming, cationic polymerization and alkylation. The relationships between the activity and acidity of these catalysts,¹⁻⁴ the presence of hydroxyl groups originating from chemisorbed water⁵⁻⁶ and speculations on the nature of acid sites with reference to the hydroxyl groups⁷⁻⁸ have been the subject of numerous investigations. While a clear-cut picture about the origin, the diversity in the observed effects of various types of acid sites and their inter-relationship is yet to emerge, it has more or less been established that presence of small amounts of water affects the catalytic activity of these oxides^{5, 6, 9}.

Finch and Clark⁶ have reported that for the isomerization reaction of 1-butene over silica-alumina, more than 0.45 per cent water is necessary, which acts cooperatively with a complex for polymerization. Similarly, Hindin *et al*² also observed that addition of 0.05 per cent water gives an active isomerization catalyst. Maciver¹⁰ has reported the initial development and subsequent loss of acidity as measured by ammonia adsorption, during the dehydration of γ -alumina. Yamadaya *et al*¹¹ attributed observed basic property of alumina to weakly adsorbed free hydroxyl groups and not to the remaining hydroxyl groups on the surface after dehydration, on the basis of the observa-

tion that basic property begins to appear when water corresponding to monomolecular layer adsorption was adsorbed and becomes constant with adsorption of water corresponding to termolecular layer. An interesting correlation between the amount of water adsorbed on alumina and basicity of surface was also found by Tanabe *et al*¹², who demonstrated a sharp increase in basicity with amounts of adsorbed water. The effect of water on acid strength distribution in alumina and silica-alumina, as studied by Hirschler,¹³ suggests the occurrence of different kinds of acid centres on the surface.

In spite of many observations like those noted above, no serious attempt has been made to relate the water adsorption with the surface acidity or basicity. Recently, the water adsorption property of silica, alumina and silica-alumina and the relation between the amount of physisorbed and chemisorbed water have been described in details by Morimoto *et al*¹⁴ but the effects of adsorbed water on the surface acidity has not been discussed. The purpose of the present work is to investigate the relationship between the water adsorption and acidity or basicity as observed in silica, alumina, silica-alumina catalysts.

Experimental

(1) Materials

Alumina I: To a solution of aluminum nitrate, a solution of ammonium bicarbonate was slowly added with vigorous stirring room temperature. The pre-

precipitate was washed with distilled water till free from nitrate ions, and was dried in an air oven at 110°C for 72 hours. The dried material was size between 16-20 mesh (BSS) and used for several experiments.

Alumina II : Aluminum nitrate solution was slowly added to ammonium bicarbonate till the final pH of solution is 7.0. This method yields alumina having lesser micropores. The precipitate was similarly washed, dried and sized as alumina I.

Silica : Sodium silicate (sp. gr. 1.18) was slowly added to 500 ml. 10 per cent, hydrochloric acid solution till the final pH of the solution was 0.5. The gelation was done at 60°C which took 75 min. approximately. The gel was washed with water till free from chloride ions. and then dried and sized as above.

Silica-alumina : Silica gel was prepared by addition of sodium silicate (sp. gr. 1.15) to a dilute sulphuric acid (4.6 per cent) solution at 12°C and pH 5.0. The air-dried gel was soaked in 0.1 N sulphuric acid and supernatant liquid was drained. The operation was repeated four times and the gel then washed with distilled water till free from sulphate ions. To this gel the required amount of aluminium nitrate was added and the fine paste was suspended in water. The suspension was stirred and ammonia (1.5 N) was added till pH 8.5. The gel was filtered and washed till free of nitrate ions and dried at 110°C sized.

(2) Measurements

Surface Area : Pore Size Distribution and Pore Volume : The surface area was determined by BET method, pore volume by helium and mercury displacement and pore size distribution by an Aminco porosimeter.

Water Content : This was determined by successive loss on ignition method¹⁵.

Water Vapour Adsorption : The samples calcined at 500°C were evacuated at 400°C for 2 hours. The water vapour absorption isotherm was obtained by the gravimetric method using an apparatus described earlier.¹⁶

DTA : Thermograms were obtained in an assembled DTA unit employing a Gallenkamp horizontal furnace with silica sample holders a Bausch and Lomb recorder and other transitrol programmer.

Acidity and Basicity : Exchangeable acidity was determined by allowing the sample to remain in contact with the solution for nearly 2 hours with occasional shaking, and titrating the acid with standard alkali, or by measuring pH of solution.

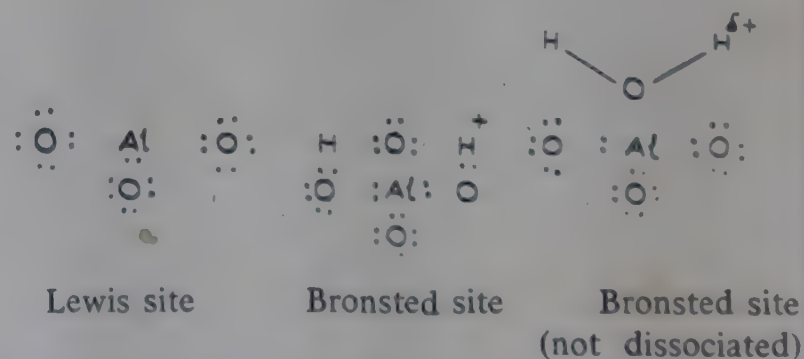
Hammett acidity of the samples was determined by several indicators (Table 2) by the method of Tamele³. Acidity was titrated with standard n-butylamine and basicity with benzoic acid.

Results & Discussion

Alumina : The physico-chemical properties, water content, basicity and acidity of the two samples are summarized in Tables 1—3.

The samples calcined at different temperatures, representing different degree of hydration, showed marked basic character along with weak acidity. Both the acidity¹⁷⁻¹⁸ and basicity¹¹⁻¹² in aluminas have been observed by many workers. Some authors^{19,20} have assigned a neutral or an amphoteric surface to alumina. It appears that this property of alumina surface is determined by the method of preparation which affects the relative distribution of acidic or basic sites resulting in a neutral, acidic or basic surface.

The hydrated forms of alumina are generally boehmite, bayerite and hydrargillite which on heating results in γ -alumina and α -alumina depending upon the temperature. The ability of aluminum ion to exist in 4 and 6 co-ordinated state and to absorb water in the form of hydroxyl groups results in a very complex surface structure. The acidic sites probably originates from incompletely co-ordinated aluminum-atoms, and such lattice defects provide a localized electron acceptor site resulting in Lewis or Bronsted acid sites depending upon the degree of hydration.



The basic sites on the surface of alumina, may be due to the negatively charged oxygen atom, the formation

TABLE 1

Sl. No.	Sample	Calcination Temp., °C	BET Surface Area, m ² /g.	Total Pore Volume, c.c./g.	V _m (Water adsorption) ml.	OH Groups per 100A ²	Pore Size Distribution				
							4-175	175-300	300-400	400-500	500-75000
1.	Alumina-I	100 500 900	199.3 201.4 90.3	— 0.380 —	— 0.19 —	— 13.3 —	— 97.2 —	— 0.6 —	— — —	— — —	— 2.2 —
2.	Alumina-II	100 500 900	506.8 329.8 134.4	— 1.91 —	— 0.145 —	— 13.9 —	— 43.1 —	— 10.5 —	— 6.5 —	— 5.9 —	— 34.0 —
3.	Silica	100 500 900	636.9 468.7 240.9	— 0.1605 —	— 0.038 —	— 6.3 —	— 95.3 —	— 1.2 —	— 1.2 —	— — —	— 2.3 —
4.	Alumina-Silica	100 500 900	288.9 355.2 102.8	— 0.146 —	— 0.11 —	— 9.1 —	— 95.3 —	— 2.4 —	— — —	— — —	— 2.3 —

TABLE 2—HAMMETT ACIDITY OF ALUMINA, SILICA AND SILICA-ALUMINA

Sl. No.	Indicator	PK Value	Alumina I			Alumina-II			Silica			Alumina Silica		
			100°C	500°C	900°C	110°C	500°C	900°C	110°C	500°C	900°C	110°C	500°C	900°C
1.	Benzal Acetophenon	—5.6	Basic*	Basic*	Basic*	Basic*	Basic*	Basic*	Basic*	Basic*	Basic*	Basic*	Acidic (0.3)	Acidic (0.24)
2.	Benzene Azodiphenylamine	+1.5	Abnormal	Acidic	Acidic	Abnormal	Abnormal	Abnormal	Acidic (0.17)	Acidic (0.36)	Acidic (0.18)	Acidic (0.17)	Acidic (0.61)	Acidic (0.60)
3.	p-Dimethylaminoazobenzene	+3.3	Basic*	Basic*	Basic*	Basic*	Basic*	Basic*	Acidic (1.0)	Acidic (0.66)	Acidic (0.40)	Acidic (0.61)	Acidic (1.1)	Acidic (0.49)
4.	A-naphthyl red (Phenyl azonaphthylamine)	+4.0	Basic*	Slightly acidic (0.01)	Basic*	Basic*	Basic*	Basic*	Acidic (0.34)	Acidic (0.75)	Acidic (0.25)	Acidic (0.47)	Acidic (0.80)	Acidic (0.67)
5.	Methyl Red	+4.8	Basic (0.09)	Basic (0.14)	Basic (0.09)	Basic (0.43)	Basic (0.32)	Basic (0.25)	—	—	—	—	—	—
6.	Neutral Red	+6.8	Abnormal	Abnormal	Acidic	Abnormal	Abnormal	Abnormal	Acidic (0.77)	Acidic (0.52)	Acidic (0.11)	Acidic (0.21)	Basic	Basic
7.	Phenolphthalein	+9.3	Acidic (0.09)	Acidic (0.46)	Acidic (0.03)	Acidic (0.72)	Acidic (2.62)	Acidic (1.24)	—	—	—	—	—	—

*Titration with benzoic acid results in desorption of indicator from the surface prior to change in colour.

*The values in bracket denote acidity or basicity in meq./g.

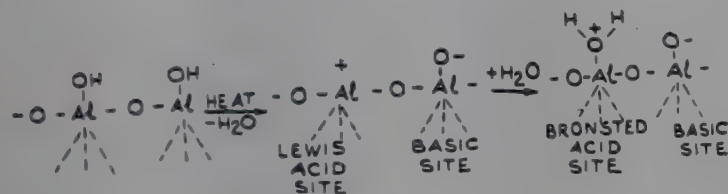
TABLE 3—EXCHANGE ACIDITY OF ALUMINA, SILICA AND SILICA-ALUMINA

Sl. No.	Exchange Material	Alumina-I			Alumina-II			Silica			Alumina-Silica		
		110°C	500°C	900°C	110°C	500°C	900°C	110°C	500°C	900°C	110°C	500°C	900°C
1.	KCl	Acidic (0.46)	Acidic (0.09)	Acidic (0.006)	Acidic (0.22)	Acidic (0.16)	Acidic (0.13)	Acidic (0.026)	Acidic (0.013)	Acidic (0.009)	Acidic (0.35)	Acidic (0.45)	Acidic (0.013)
2.	NaCl	Neutral	Neutral	Neutral	Neutral	Neutral	Neutral	Acidic (0.016)	Acidic (0.009)	Acidic (0.003)	Acidic (0.006)	Acidic (0.009)	Acidic (0.004)
3.	NH ₄ C ₂ H ₃ O ₂	Basic (7.57)*	Basic (7.98)*	Basic (8.05)*	Basic (8.1)*	Basic (7.94)*	Basic (7.94)*	Acidic (0.03)	Acidic (0.06)	Acidic (0.016)	Acidic (0.20)	Acidic (0.03)	Acidic (0.005)
4.	(NH ₄) ₂ C ₂ O ₄	Basic (0.17)	Basic (0.20)	Basic (0.16)	Basic (0.14)	Basic (0.23)	Basic (0.15)	Acidic (0.046)	Acidic (0.037)	Acidic (0.009)	Acidic (0.4)	Acidic (0.48)	Acidic (0.002)

*Values in brackets denote acidity or alkalinity in meq./g.

*Only pH of solution was measured.

of which has been shown schematically by Tanabe *et al*¹² as follows :



The free hydroxide ions on the surface of alumina are also basic site and this basicity as well as protonic acidity (Bronsted) can be estimated by exchange of respective ions with anions or cations of electrolytes. The indicator method gives the total acidity or basicity by using suitable indicators and titrating with a base (*n*-butylamine) or acid (benzoic acid) in non-aqueous medium, as the case may be.

The surface of alumina may thus be conceived as comprising several types of acid and basic sites and it has been the purpose of several investigations to find out precisely the number and strength of such sites and their origin.^{7, 21}

The results (Tables 2 and 3) demonstrated the existence of both acid and basic sites on the surface of alumina, upto 900°C. The aluminas under investigation contained quite appreciable amounts of adsorbed water. In alumina I, the physisorbed water was expelled around 200°C and chemisorbed water was continuously evolved between 410 and 600°C as observed in DTA thermogram (AI) (Fig. 1). The loss of adsorbed water in alumina II, was however completed around 400°C (Fig. 1, AII) which was due to greater number of macropores (Tables 1) resulting from different method of preparation of this sample. The amount of exchangeable acidity (Bronsted sites)

was also more in alumina II than alumina I (Table 3), which supported the findings of Fiumara *et al*,²² viz., acidity is less in highly microporous alumina.

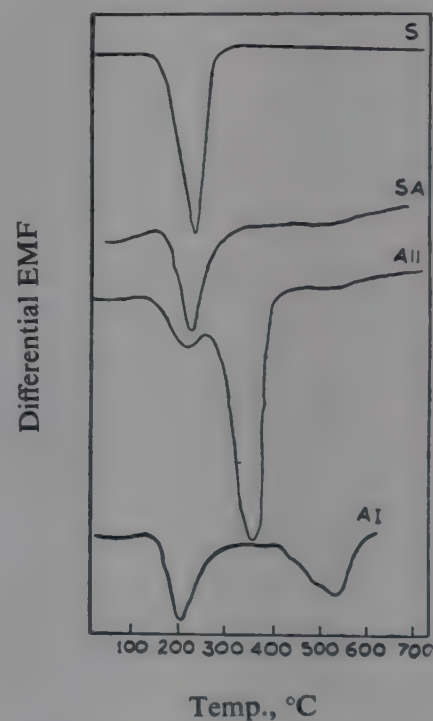


Fig. 1—DTA of Different Samples AI-Alumina (I); AII-Alumina (II); S-Silica; SA-Silica-Alumina

Aqueous electrolytes reacts with surface of alumina by ion-exchange with surface Al³⁺, surface OH' H⁺ on surface hydroxyl groups or impurities. The exchange properties of alumina was studied by using four, different electrolytes (Table 3) and it can be seen that all kinds of behaviour were observed. With potassium chloride some proton exchange occurs and observed acidity decreases with the increasing temperature of calcination. With sodium chloride no exchange occurs at all and with ammonium acetate and ammonium oxalate exchange

occurs with hydroxide ions (basic sites). Unlike the acidity, exchangeable basicity of maximum in the samples calcined at 500°C. Pines and Haag²³ found no exchange occurring with sodium chloride and ammonium acetate and Hirschler *et al*¹³ concluded that Bronsted-like site do not behave as simple free protons readily exchangeable, and that the nature is much more complex. The exchange adsorption of cations from electrolytes is generally believed to be governed by the magnitude of their charges, and by radii of their ions. This, however, simply fails to explain the observed proton exchange with only potassium chloride and hydroxide ion-exchange with ammonium acetate and ammonium oxalate. It appears that besides the charge magnitude and ionic radii of ions of electrolyte, the strength and location of protons and hydroxide ions on alumina surface are the determining factors in exchange method of estimation of acidity. However, the above results obtained with electrolytic exchange method should be viewed with caution since water is likely to react with some surface sites resulting in the formation of additional protons and hydroxyl ions.

Besides the exchangeable acidity, the various Hammett indicators used also give basic colour as well as acid colours with the aluminas (Table 2). The acidity of alumina determined by titration with *n*-butylamine is maximum in the samples calcined at 500°C. A similar trend is observed with the basicity determined by benzoic acid titration using methyl red indicator. The basic colour observed with indicators having lower pH value get desorbed when titrated with benzoic acid, and it was very difficult to detect the end-point which indicates that the hydroxyl groups which give basic colour with indicators in this range are weakly adsorbed on the surface.

(i) The acid and basic sites co-exists on the alumina surface at all temperatures; (ii) active exchangeable protons as well as hydroxide ions are present on the surface; (iii) the acid and basic sites of different strength are present; and (iv) relative abundance of acid sites and basic sites varies with the water content.

At lower temperature, the aluminas contain sufficient water to form a monolayer on the surface. In the alumina calcined at 500°C also, there is an appreciable amount of adsorbed water which remains in the form of isolated hydroxyl groups. It is apparent that observed basicity and acidity is mainly due to hydroxide ions and protons derived from the

adsorbed water molecules. The dual role of adsorbed water in promoting basic sites as well as acid site is perhaps related with the surface defect structure of alumina. This is clear from the fact that in aluminas I and II, calcined at 500°C, though the water contents are nearly same (13.3 and 13.9 OH groups/100 Å²), they very much differ in their total content of acidity or basicity. It is also apparent that though the acidity or basicity is dependent on the water content, it does not bear a direct quantitative relationship, and important point in this regard is the distribution of water on specific sites on the surface of alumina.

Water Vapour Adsorption and Acidity: The effect of water on acidity has been studied in details by carrying out water vapour adsorption over aluminas at different partial pressures and measuring the acidity at corresponding partial pressures.

The water vapour adsorption isotherms over the alumina samples cured at 500°C (Fig. 2), belonged to the II-type of Brunauer's classification.¹⁴ The V_m (monolayer capacity), as calculated from BET plot of water adsorption data, a value of 0.19 ml/m² and 0.145 ml/m² for aluminas I and II respectively. At the relative vapour pressure corresponding to V_m , it

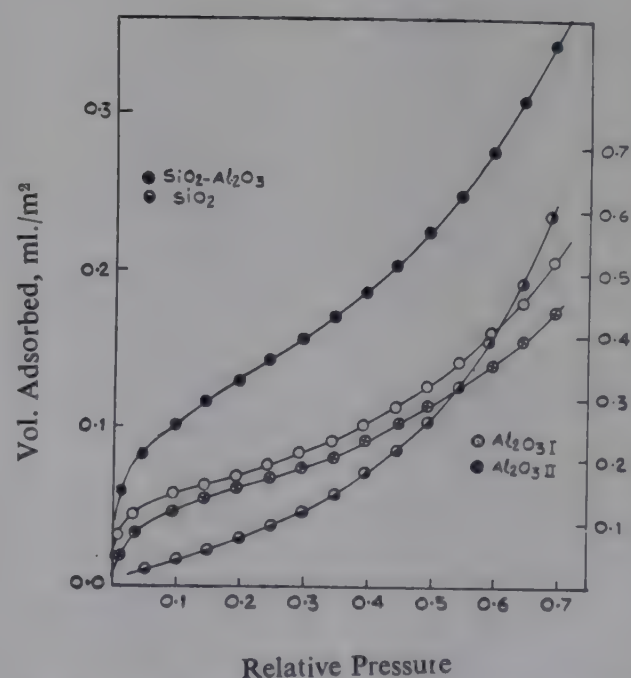


Fig. 2—Water Vapour Adsorption Isotherm on Alumina, Silica and Alumina-Silica.

was assumed that the surface was completely covered with water molecules. The initial water content of the samples at 500°C before water vapour adsorption was 13.3 and 13.9 OH groups/100 Å². The initial water contents of the samples at 500°C are nearly equal to these values. Morimoto *et al*¹⁴ found that

at all temperatures the water was physisorbed as well as chemisorbed on the surface of alumina and their ratio was equal to 0.5 ($\text{H}_2\text{O} : \text{OH} = 0.5$ approx.). Thus, the water content, 13.3 and 13.9 $\text{OH}/100 \text{ \AA}^2$ of aluminas I and II respectively represent the half of this as chemisorbed and half as physisorbed. The fact that further adsorption of water occurred and from the V_m value it can be easily seen that at 500°C the surface was not covered with a monolayer though the water content was nearly equal to the theoretical monolayer value, 12.5 $\text{OH}/100 \text{ \AA}^2$. The physisorbed water therefore may be assumed to be lying on the chemisorbed water, which covers nearly half of the surface at 500°C .

The acidity and basicity of aluminas, as a function relative vapour pressure of water (Fig. 3) was found to be increasing upto the formation of monolayer. It implies that hydration of alumina surface occurred resulting in additional basic and acid sites.

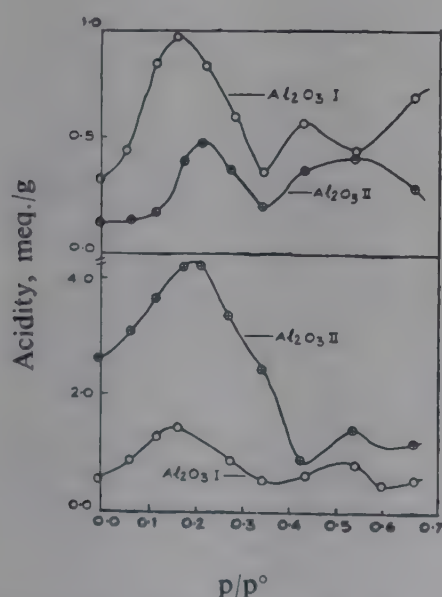


Fig. 3—Relationship between Water Vapour Adsorption and Acidity/Basicity in Alumina.

The heating of hydrated aluminas at around 500°C may result in a surface which may be either acidic and/or basic or neutral or amphoteric. It may depend upon several factors, e.g. the number of Bronsted site, Lewis site and defects introduced in the arrangement of oxide and aluminum ions in the top layer, the occurrence of strained Al-O-Al linkages and the charge density of the various types of isolated hydroxyl groups postulated by Peri.^{7, 21} The origin and co-existence of acidic and basic sites can be explained easily on the basis of Peri's model²¹ of γ -alumina surface as well as from the Al-O-Al linkages as shown by Tanabe.¹²

In conformity with the experimental results, the surface of alumina I at 500°C before water vapour adsorption, may be conceived as represented in Fig. 4(A), which was predominantly basic (larger concentration of type A and D hydroxyl groups) with few acidic hydroxyl groups (type B, E and C sites). Besides these, there may be basic sites due to negatively charged oxygen atoms. Hydration of this type of surface results in an increase in basicity as well as acidity up to the formation of monolayer as is evident from Fig. 3.

The water is both physisorbed as well as chemisorbed on the surface of alumina. The chemisorbed water in the form of hydroxyl groups which are held by aluminum atoms may be responsible for the observed increase in basicity. All the five types of sites proposed by Peri are likely to maintain their respective basic or acidic character even in the completely hydrated state. This is because the environment of for example type 'A' site only changes from negative O^- to negative OH^- , which is only likely to affect the strength of 'A' site but not its inherent basic character (Fig. 4B). However, oxide ions surrounded by positive aluminum atoms, on hydration may result in the formation of acidic site (Type C) resulting in increase in acidity.

The increase in acidity as well as basicity up to V_m may be also due to the physisorbed water molecules on the surface hydroxyl groups. The physisorbed water molecules due to dipole interaction tendency to displace lone pair of electrons from oxygen atom

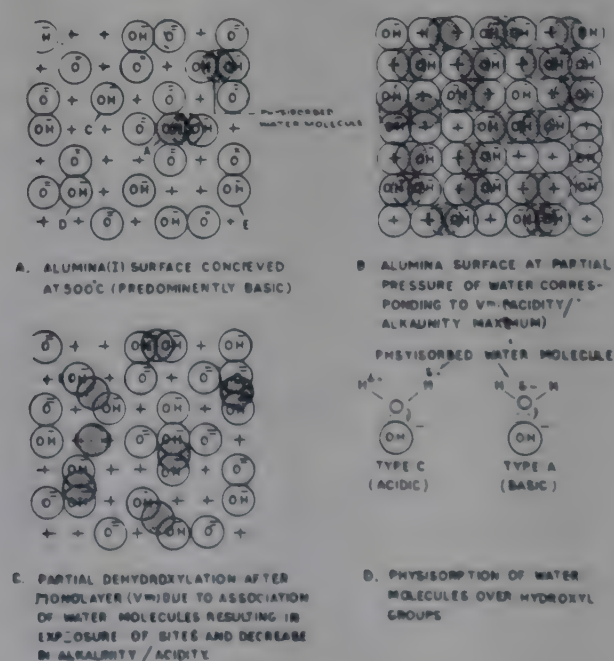


Fig. 4—Relation between Water Vapour Adsorption and Acidity/Alkalinity over Aluminas.

of hydroxyl ions may assume a feeble acidic or basic character (Fig. 4D), the proton of water molecule adsorbed on type C site being more active (acidic site) than the proton on type A site (basic site).

After the adsorption of water equivalent to monolayer capacity, the acidity and basicity has been found to decrease (Fig. 3) sharply. This is perhaps due to the coverage of comparatively strong acidic and basic sites of the surface with physisorbed water molecules thus rendering them inactive. Since the physisorbed water molecules display only feeble acidic or basic character, the result is total decrease in acidity and basicity. At still higher relative vapour pressure, the physisorbed water molecule probably association through hydrogen bonding on the surface and this association results in exposure of the original sites, with the result in increase in acidity and basicity, as experimentally observed (Fig. 3) which is represented in Fig. 4C. At still higher relative vapour pressure more physisorbed water molecules may again cause a decrease in acidity and alkalinity, and if further association may occur, a continuous increase and decrease will be the result which is, in fact, observed experimentally. This process may continue till finally the surface is completely covered with molecular water and acidity or basicity may attain a constant value.

Silica and Silica-Alumina: The silica and silica-alumina were generally strongly acidic, bronsted sites prominent in hydrated state and Lewis site in the dehydrated state. With all the exchangeable materials, only acidic behaviour are observed (Table 3) unlike as in aluminas. The exchangeable acidity generally decreases with the increasing temperature in case of silica, while in silica-alumina, it is observed maximum in sample calcined at 500°C which is in accordance with the results of many published work²⁻⁶.

Though generally strongly acidic, the silica and silica-alumina possesses acidic sites of various strength and basic sites also. The strong acid sites may not be affected by water adsorption to the extent the weak acid sites are likely to be affected. The indicators employed in this investigation are having higher pK values which give acid colours with either medium or weak acid sites and as the results in Table 2 indicate quite appreciable amount of acidity is observed with these indicators. The basic colour of benzol acetophenone persists with silica at all temperatures and with silica-alumina samples cured at 110°C. With the increasing temperature of calcination silica-

alumina gave acid with benzalacetophenone. Acidic sites observed with neutral red are converted to basic sites (Table 2) in silica-alumina calcined at higher temperature.

The basicity of silica may be related with some structural defects resulting into negatively charged oxygen sites. In silica-alumina, this may be due to hydroxyl ions on alumina or structural basicity. Both the possibilities seems to be there, since with benzal acetophenone the basic character disappears with the increasing temperature, and with neutral red the basic character appears in the sample calcined at higher temperature, which also indicates that existence of $Al^{+}O^{2-}$ Al^{+} sites may not be ruled out.

The water content of silica is found to be 6.3 OH/100 Å² in the sample cured at 500°C. Most of this water may be only chemisorbed, since in silica, physisorption of water occurs only during the water vapour adsorption experiment¹⁴. The water adsorption isotherm on silica is shown in Fig. 2, which is type III as obtained by Morimoto *et al*¹⁴. The Vm value calculated is 0.038. The physisorption of water occurs only on the surface hydroxyl groups.

The acidity plot as a function of relative vapour pressure shown in Fig. 5 indicates increase in acidity up to the formation of monolayer. This increase may be due to the hydroxylation of dehydroxylated sites. On further adsorption beyond monolayer coverage, the acidity decrease sharply as observed in the case of alumina also. Similar explanation may be given for silica, that the physisorbed water on the acidic sites reduces their acidity. With further increase in partial

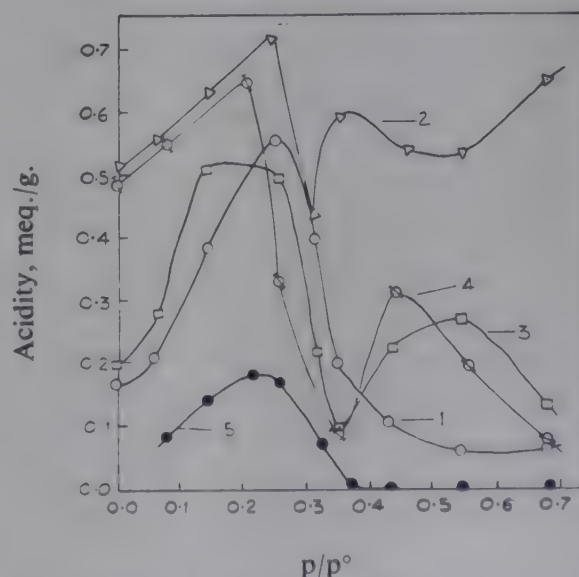


Fig. 5—Relation between Water Vapour Adsorption and Acidity in Silica. 1. Benzene Diphenyl Amine. 2. Neutral Red. 3. Butter Red. 4. Dimethyl Aminsdo Benzene. 5. A. Naphthyl Red.

pressure of water, acidity once again increases, which may be due to the aggregation of water molecules and exposure of sites. This process is repeated as is evident from number of peaks and depression observed in acidity plot (Fig. 5).

In silica-alumina again type II adsorption isotherm is observed (Fig. 2) as in case of alumina. The water adsorption bears a similar relationship with acidity (Fig. 6) as in the case of silica and aluminas.

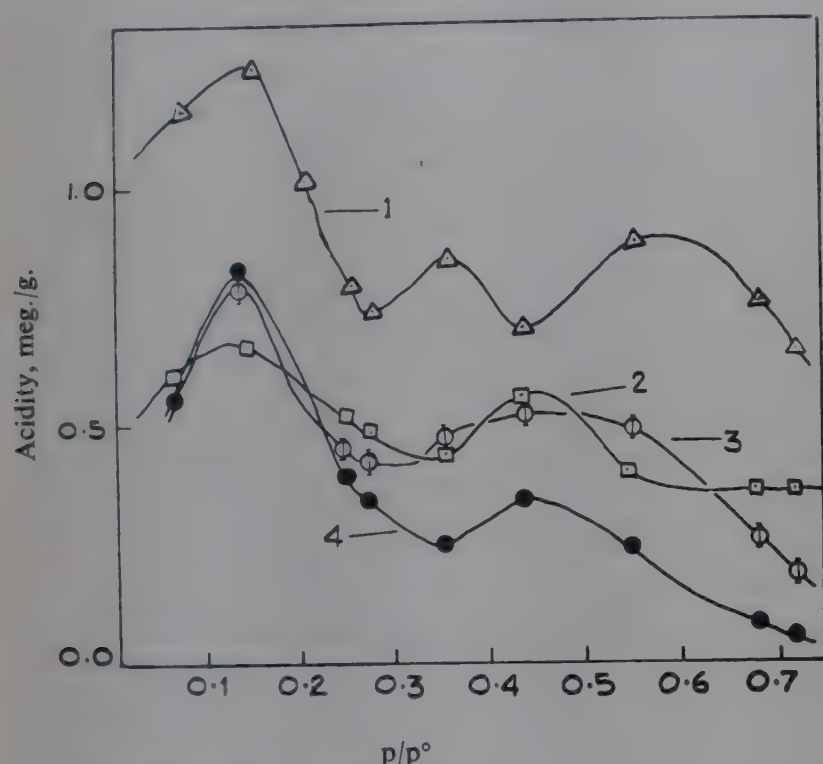


Fig. 6—Relationship between Water Vapour Adsorption and Acidity in Silica-Alumina. 1. Neutral Red. 2. Bitter Yellow. 3. Dimethyl Aminobenzene. 4. A Naphthyl Red.

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The state of metal dispersion in a γ -alumina supported platinum catalyst and the effect of heat treatment have been investigated by chemisorption studies. During heating, the platinum crystallites grow with a consequential decrease in H/Pt atom ratio. It has been confirmed that the isothermal decrease of platinum area follows a second order reaction rate mechanism. Since measurement of metal areas as small as in the present case involves uncertainty in accuracy, an attempt has been made to substitute in the rate equation the total area instead of metal area. It has been established that the new expression $\frac{1}{S_{\text{BET}}} = \frac{1}{S_0} + K_1 t$ can also be used to describe the sintering rate process. In yet another rate expression the time 't' has been substituted by temperature of sintering 'T'. The validity of the expression $\frac{1}{S_{\text{BET}}} = \frac{1}{S_0} + K_2 T$ has been verified experimentally.

Temperature Dependence of Active Surface Area of Platinum Catalyst*

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The small amounts of platinum used in most catalysts are too small to cover a sizeable fraction of the high surface support. Therefore, it is imperative in investigation on catalysis to estimate the proportion of the total surface area active in catalytic reaction. In general, the degree of dispersion of platinum has been estimated¹ by either hydrogen or carbon monoxide chemisorption. This information not only helps in determining the time required for the contaminants in the reactant gases to poison the active surface, but also in assessing and selecting such catalysts.

It is known¹⁻² that platinum sizes in the reactor grow from 10-20 to 100-300 Å. Sintering is considered to be the main factor responsible for the growth in the platinum sizes which upsets the activity and selectivity of the catalysts. The present investigation has been taken up to determine how thermal treatment affects dispersion, and whether sintering follows any rate process.

Experimental

The fresh commercial catalyst used was a platinum

catalyst supported on γ -alumina having a platinum content of 0.6 per cent.

Pre-treatment of Catalysts: Two sets of samples were prepared. In one set, the samples were treated at 700°C for 2, 6, 12, 22 and 42 hours and in the other, they were thermally treated for 6 hours at 600, 650, 700 and 800°C.

The gases used were hydrogen for catalyst reduction and adsorption, nitrogen for BET surface area determination and spectroscopically pure helium for dead space determination. Commercially pure hydrogen was purified by passing over a De-oxo catalyst and then dried by passing it over magnesium-parchlorate. Nitrogen was passed through reduced copper at 500°C and dried over liquid nitrogen trap.

A conventional volumetric glass apparatus³ was used for the adsorption measurements. The catalyst was treated in the following manner prior to hydrogen chemisorption: The sample was out-gassed at 300°C for nearly 4 hours and then reduced in a stream of hydrogen at 250°C for 1 hour. Finally, the reduced sample was degassed at 350°C for 6-8 hours to a vacuum of 10^{-5} mm. Hg. and degassing was taken to be complete when a pressure of less than 10^{-3} torr could be maintained for nearly half-an-hour in the system after disconnecting it from the pumps.

* This paper was presented at the Symposium on Science of Catalysts and Its Application held at Banaras Hindu University, Varanasi (U.P.) on March 28-30, 1973.

Platinum crystallite sizes were evaluated from the hydrogen chemisorption data.

Results and Discussion

Hydrogen sorption on the untreated catalyst was measured at 250°C and different pressures. The results are shown in Table 1. The adsorption data have been fitted in the transformed¹ form of the Langmuir equation:

$$\frac{1}{V} = \frac{1}{V_{mb}} \times \frac{1}{p^{\frac{1}{2}}} + \frac{1}{V_m}$$

TABLE 1—ADSORPTION ISOTHERM DATA AT 250°C FOR THE FRESH CATALYST

P, cm.	V at NTP/2 g. Cat., c.c.	1/V, c.c. ⁻¹	1/P ^{1/2} , cm. ^{-1/2}
10.1	0.32	3.10	0.30
16.9	0.43	2.30	0.24
24.1	0.54	1.84	0.20
31.5	0.62	1.60	0.18
35.3	0.70	1.42	0.17
46.7	0.78	1.28	0.15

where V is the volume of gas adsorbed at pressure p, V_m the volume corresponding to a monolayer, and b a constant.

In case the equation is obeyed, a plot of $\frac{1}{V}$ against $\frac{1}{p^{\frac{1}{2}}}$ should give a straight line, from which values of V_m and b can be calculated. It is evident from the linear plot in Fig. 1 that the adsorption conforms to the Langmuir equation upto the range studied. The validity of the Langmuir's equation at 250°C suggests that the adsorption is predominantly of chemisorption type.

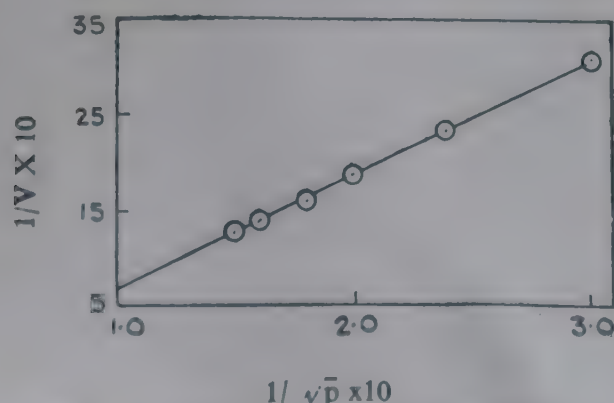


Fig. 1—Langmuir Isotherm for Hydrogen Adsorption at 250°C

The adsorption measurement were carried out at 240 mm. pressure and 250°C. It has been shown¹ that essentially complete surface coverage is achieved on platinum under these conditions. The number of hydrogen atoms adsorbed per platinum atom, platinum area and particle size as calculated from the adsorption data are shown in Tables 2 and 3. The platinum metal area was calculated by using the following equation suggested by Spenadel and Boudart¹.

$$S = \frac{X \times 6.02 \times 10^{23}}{195.09 \times 1.12 \times 10^{15} \times 10^4}$$

TABLE 2—CHEMISORPTION DATA OF CATALYST SAMPLES HEAT-TREATED AT 700°C FOR VARYING PERIODS

Sample No.	Heat Treatment at 700°C, hr	S _{BET} , m ² /g.	H ₂ Chemisorbed on Pt., c.c. NTP/g.	H. Atom Chemisorbed per Pt. Atom, X	Pt. Surface Area, m ² /g. Pt.	Average Platinum Size, Å
1.	0	352.0	0.291	0.845	232.8	10.0
2.	2	196.0	0.102	0.296	79.1	29.4
3.	6	169.5	0.083	0.241	66.6	34.9
4.	12	146.2	0.061	0.178	49.0	47.4
5.	22	120.0	0.039	0.116	33.2	72.7
6.	42	88.5	0.025	0.072	19.8	117.4

TABLE 3—CHEMISORPTION DATA OF CATALYST SAMPLES HEAT-TREATED FOR 6 HOURS AT DIFFERENT TEMPERATURES;

Sample No.	Heat Treatment for 6 Hours C	S _{BET} m ² /g.	H ₂ Chemisorbed on Pt., c.c. NTP/g.	H. Atom Chemisorbed per Pt. Atom, X	Pt. Surface Area, m ² /g. Pt.	Average Platinum Size, Å
1.	600	272.3	0.133	0.386	106.4	21.4
2.	650	198.2	0.094	0.274	75.5	30.8
3.	700	169.5	0.083	0.241	66.6	34.9
4.	800	132.5	0.010	0.031	38.5	60.4

where S is the platinum surface area in m²/g. and X is the hydrogen atom adsorbed per platinum atom. The platinum crystallite sizes have been calculated from the hydrogen chemisorption data by employing the relationship:

$$S = \frac{5}{d\rho},$$

where S is the platinum surface area, 'ρ' the platinum density and 'd' diameter of the platinum crystallite size. The above calculation is based on the assumptions of Hermann *et al*⁴ and other workers⁵, which

are : (1) the γ -alumina carrier does not chemisorb hydrogen, and (2) platinum crystal is a cube with five exposed faces having the sixth face in contact with the support.

It can be seen from Table 2 that with the gradual increase in the time of heat treatment at 700°C, the extent of sintering increases which is reflected in a decrease in the BET and the platinum area and a consequential increase in the platinum crystallite sizes. In the case of the catalyst sintered at 700°C for varying period, the BET area and platinum area have gone down from 352 to 88.5 m²/g. and 232.8 to 19.8 m² respectively and the average platinum size has increased from 10 to 117.4 Å at 42 hours' treatment. A similar type of change is observed when the catalyst is sintered at different temperatures (Table 3) for a fixed time. Here again the platinum area drops down from 106.4 m²/g. at 600°C to 38.5 m²/g. at 800°C and platinum crystallites increases from 21.4 to 60.4 Å for the same range. It is evident from the above tables that sintering of platinum catalyst whether for different period at the fixed temperature or at different temperatures for a fixed time results in decrease in platinum metal as well as the total surface area and growth of the platinum crystallites. Maat and Moscou⁵ has, however, reported that the heating of platinum catalyst at 780°C does not cause any appreciable change in the surface area of alumina support. This implies, therefore, that in an isothermal sintering at 700°C, as in the present case, any change in the surface area should be mainly due to change in the platinum area. If it was so, the total surface area (Table 2) should have remained fairly constant as the metal area is too small to reflect any appreciable change in the surface area. In this study a drastic reduction both in the metal as well as surface area has been observed (Table 2), which suggests that the surface area of alumina support is also affected due to sintering.

Sintering has been considered a process involving an energy barrier⁶, so that the rate is a function of both time and temperature. The different rate expressions⁷⁻¹¹ for sintering in relation with variation in grain size, pore diameter, density and surface area, etc. are based on the studies at a constant temperature and varying time. Much less attention has, however, been paid towards the study of sintering rates as a function of temperature. Maat and Moscou⁵ and Hermann *et al*⁴ have shown that the sintering of the platinum on alumina catalyst follows a second order

reaction. However, they studied the sintering mechanism at fixed temperature for varying time only. The equations for the first and second order reactions are :

$$\text{1st order : } \ln S = \ln S_0 - Kt \quad \dots\dots\dots(1)$$

$$\text{2nd order : } 1/S = 1/S_0 + Kt \quad \dots\dots\dots(2)$$

where K is sintering rate constant, S the platinum surface area and t sintering time. The validity of the above two equations have been verified by studying the kinetics of sintering at 700°C. The plots of 1st and 2nd order sintering reactions are presented in Figs. 2A and 2B, and the straight line obtained in Fig. 2B confirms that the sintering rate process is of second order.

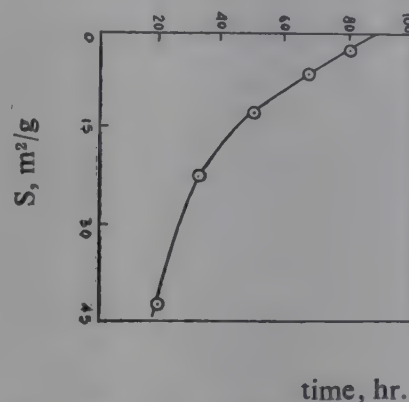


Fig. 2A—First Order Sintering Rate

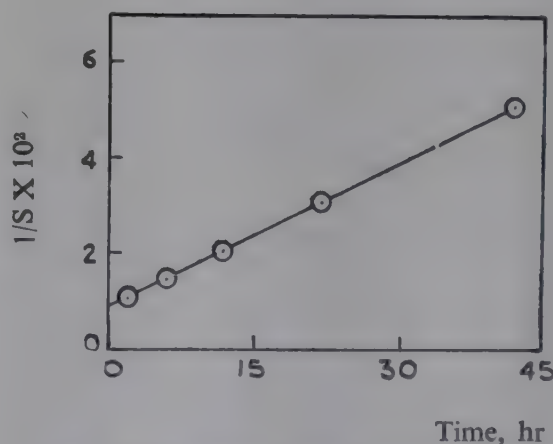


Fig. 2B—Second Order Sintering Rate

The platinum surface in the catalyst is very small and therefore only a little quantity of gas is chemisorbed which is of the order of few millilitres only even in the case of fresh catalyst. The amount is further more reduced if one is to study the gas adsorption on a thermally treated catalyst. The measurement of depleted metal area by volumetric method becomes erroneous and the errors are likely to be magnified. Keeping this in view, the present authors have modified above equation and suggested an expression involving the total surface area instead

of the metal area. Now, if the 'S' of equation (2) is substituted by S_{BET} the equation becomes:

$$\frac{1}{S_{BET}} = \frac{1}{S_0} + K_1 t \quad \dots\dots\dots(3)$$

If the above expression is obeyed, a plot of $1/S_{BET}$ Vs t should give a straight line. The validity of the expression is proved by the straight line obtained in Fig. 3.

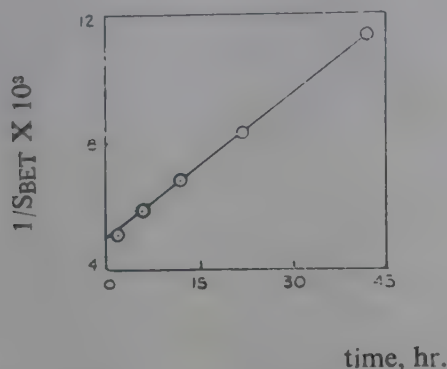


Fig. 3—Second Order Sintering Rate

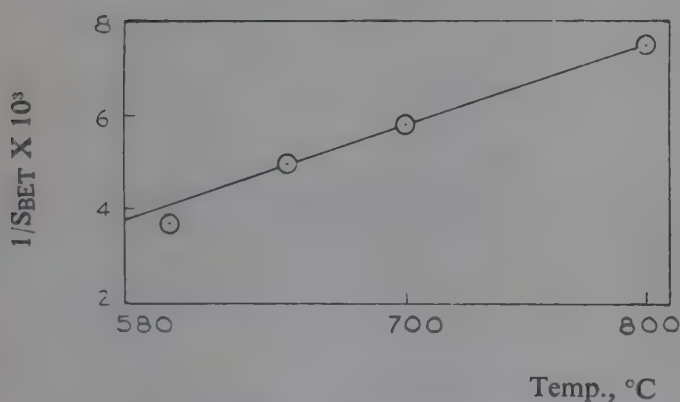


Fig. 4—Second Order Sintering Rate

Similarly, as the sintering is a function of both time and temperature, and therefore, it should be possible to evolve a rate expression involving the surface area and temperature of sintering. In this case also the time has been substituted with temperature in equation (3), the new equation being.

$$\frac{1}{S_{BET}} = \frac{1}{S_0} + K_2 T \quad \dots\dots\dots(4)$$

where T is temperature.

The straight line obtained in Fig. 4 confirms our contention that the temperature can also be used in describing the second order sintering rate process.

Conclusion

From the above discussions, it can be concluded that in a system like platinum on alumina, quantitative relationship exists between both the time and temperature with decrease in metal area during the process of sintering. It has also been shown that as the measurement of small metal area by volumetric method may not be very accurate, the total surface area can be conveniently substituted for metal area in the rate equation and the new expression has been found to be equally suitable for describing the sintering rate process.

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The on-column-catalysis technique of gas chromatography has been applied on the study of catalytic behaviour of nickel Chromosorb-P for the methanation of the oxides of carbon. The catalyst has been found to start functioning around 200°C and reach maximum activity in the region of 310-335°C accompanied by a fall in conversion efficiency at higher temperatures. The maximum capacity per gram of the catalyst at the critical temperature zone has been found to be 1.57 c.c. of carbon dioxide. The role of additional catalytic active sites has been inferred from the observation of increased methane yield with larger reactant pulses beyond the critical capacity.

A method has been proposed for the rapid prediction of gas-solid reactions, in general, based on change in the nature of the universal linear plot of logarithm of specific retention volume of one of the reactants species against the reciprocal of column temperature.

Some Aspects of Methanation of Oxides of Carbon on Nickel-Chromosorb-P Catalyst by the On-Column-Catalysis Technique of Gas Chromatography

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It has been pointed out in another study (Saha, N. C. and Mathur, D. S., unpublished work) that the GC analysis of the oxides of carbon present in trace amounts in a sample is more advantageous via their catalytic conversion to methane, whose subsequent detection by FID is thousand times or more sensitive than that of the parent compounds by TC. For the nickel-based methanation catalyst, a number of supports of different pore structure were tested, Chromosorb-P being the final choice because it satisfied all the requirements for successful reaction GC-technique. Among other advantages, Chromosorb-P enabled the lowest temperature for complete conversion. It was, therefore, considered worthwhile to study various aspects of the nickel Chromosorb-P catalyst by the on-column-catalysis technique of gas chromatography.¹

Experimental

The catalyst sieved to 60-80 mesh (BSS) was packed in a 5' × 1/8" copper tubing by the conventional GC method. This column was preceded and followed by another two columns of Porapak-T, of dimensions 5' × 1/8" and 9' × 1/8". This experimental set-up eliminated overlapping of peaks of the constituents of reactant sample and reaction products. The catalyst

column in a 3" diameter coil was housed in an oven which gave a maximum temperature of 400°C, the other two columns being maintained at the ambient. For monitoring the oxides of carbon, a thermal conductivity detector was used and for methane a flame ionization detector was arranged in a single mode of operation.

Pure hydrogen dried over molecular sieve 5Å was used as a carrier gas, the pulsed sample being injected into the column assembly by a gastight microsyringe*. The activation and reactivation of the catalyst, whenever needed, were carried out in the same set-up by passing hydrogen through the catalyst column at 350°C for 4 hour. The area under a peak which was almost symmetric in all cases was computed from the peak height multiplied by peak width at half height.

Results and Discussion

Gas Chromatographic Prediction of Catalytic Activity: The inadequacies of conventional methods for rapid and meaningful evaluation of catalyst formulations and the urgency for the application of GC techniques for the development of modern industrial cata-

* From Precision Scientific Corporation of USA.

lyst have been discussed by the present authors². It is known that the on-column-catalysis technique of GC can provide quick and reliable methods for predicting whether a porous solid will act as a catalyst for a given chemical reaction. A new idea has been put forward in this paper, based on the fact that when the packing material in a GSC column possesses catalytic activity, a deviation is likely in the universal linear plot of the logarithm of specific retention volume (V_g) against reciprocal of column temperature. Under such conditions the retention time of a compound changes because of additional reaction forces (chemical forces) being superimposed on the physisorption forces, typical of GSC.

For diagnosing a methanation catalyst, a blank support column, viz. Chromosorb-P, was used in this study. 100 μ l of carbon dioxide or methane were injected quantitatively at various column temperatures from 100 to 380°C and the resultant plots of logarithm of V_g vs $1/T$ for carbon dioxide (Fig. 1A) and methane were found to be linear over the entire temperature interval. Next, the blank support column was replaced with the main catalyst column in the same experimental set-up and a similar plot was made for carbon dioxide (Fig. 1B) for a temperature range 275–380°C. It has been observed from a separate experiment that the methanation reaction upon the nickel-Chromosorb-P catalyst starts above 215°C. Hence, in Fig. 1B the methane peak resulting from the reactant pulse of carbon dioxide was monitored. A distinct break in the linearity can be observed in Fig. 1B as compared with Fig. 1A. A critical examination of Fig. 1B reveals a linear portion for temperatures below 300°C, followed by a break in linearity and a plateau region in the approximate range 320–360°C, probably again a linear portion beyond 380°C. It may be mentioned that in the plateau region the methanation reaction is complete, no unconverted carbon dioxide peak being observed in the chromatogram. Obviously, the catalyst is most reactive in this temperature zone. As expected, the interplay of catalytic forces have caused a distinct and remarkable change in the elution pattern of the reactant pulse which may be taken as a general rule for the prediction of activity of heterogeneous catalysts.

An alternative approach to Fig. 1B is the measurement of heat of sorption (ΔH) for the reactant and product species. The variation in the ΔH with a fixed minimum value in the most active temperature

zone is a sure indication of heterogeneous catalysis on solid surfaces.

The properties of a catalyst may also be predicted by injecting pulses of one of the reaction products instead of the reactant. An extensive study is suggested for determining whether the use of a product pulse is of general validity in predicting catalytic behaviour of a solid. In the present case pulses of methane were injected into the catalyst column at different temperatures and a plot of logarithm of retention volume against inverse of temperature was drawn (Fig. 1C). In this case also, a break in the linearity was observed similar to that observed in the

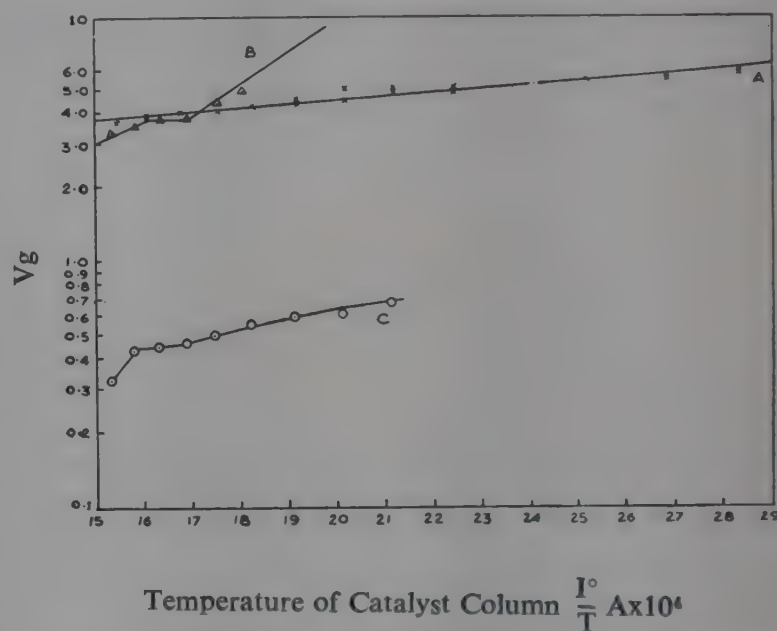


Fig. 1—Plot of Retention Volume Vs Inverse of Absolute Temperature

- A—Methane on Chromosorb P
- B—Converted Methane from CO₂ on Nickel Catalyst
- C—Methane on Nickel Catalyst

case of reactant pulse (Fig. 1B). This break in linearity indicates that the catalyst is behaving differently than a typical GSC support even to the reaction product methane which is not known to undergo any sort of chemical reaction under the conditions or show any type of chemical affinity with the support. It is, therefore, evident that there have been some geometrical transformations in the support during preparation of the catalyst. The change in the retention forces for methane can be contrasted from Figs. 1A and 1C, which were obtained for the catalyst carrier and the catalyst respectively.

Effect of Temperature on Conversion : The effect of temperature on the activity of the catalyst column upon the methanation reaction has been isolated in Fig. 2. In the first case, 400 μ l of carbon dioxide

was injected at each temperature into the column assembly and the change in the peak area of the reactant was shown in plot A and then the catalyst column was removed and the corresponding plot B was obtained for the pre-and post-catalyst columns only. It is clear from Fig. 2 that methanation reaction starts at about 200°C and the amount of residual carbon dioxide decreases rapidly upto the maximum temperature studied in this experiment.

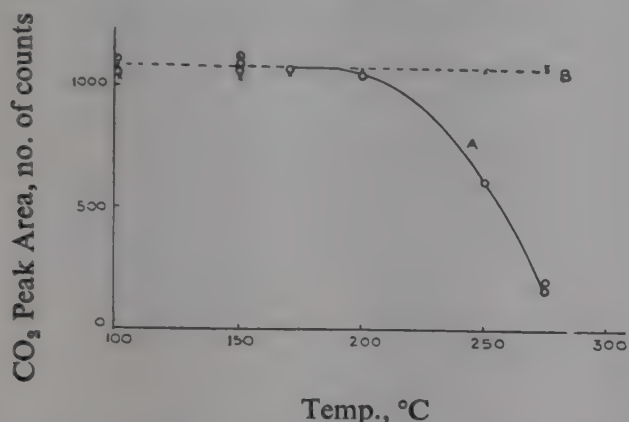


Fig. 2—Plot of Carbon Dioxide Peak Area against Temperature
A—with the Column Set-up (Porapak T5' + Catalyst 5' + Porapak T 9')
B—with the Porapak T 5' + 6" × 1/8" empty tube + Porapak T 9'

A better picture of the effect of temperature on conversion may be had from Fig. 3 where peak area for both carbon dioxide and methane were simultaneously monitored under identical experimental conditions as those of Fig. 2A. It may be noted that at 310°C and above (at least upto 335°C) there is no unconverted carbon dioxide i.e., the methanation reaction is complete or the catalyst is at its maximum activity. The portion of the plots in the temperature interval 215-300°C for both carbon dioxide and methane are not exactly symmetrical as expected, one reason being the difference of response factor of the two compounds from the thermal conductivity detector.

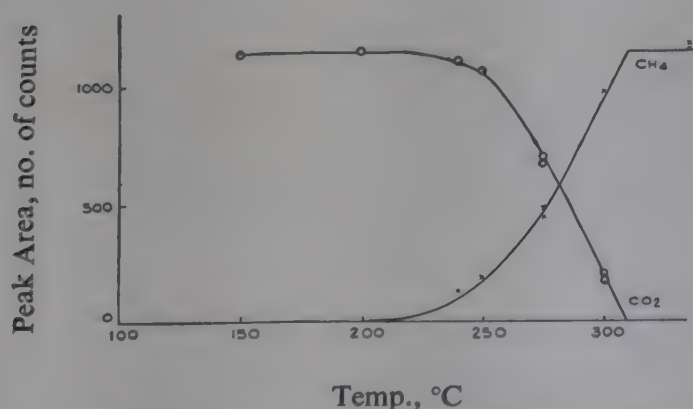


Fig. 3—Plot of Carbon Dioxide and Converted Methane Peak Area against Temperature in the Column Set-up.
[Porapak T 5' + Catalyst 5' + Porapak T 9']

Capacity of the Catalyst for Carbon Dioxide : The optimum temperature and other variables having been established, the capacity of a given amount of catalyst for accommodating the maximum amount of carbon dioxide per pulse which can be completely converted to methane was studied in Fig. 4. A linear increase in the area of converted methane for reactant sample sizes upto 3 c.c. and no carbon dioxide peak was observed in the chromatogram. Beyond 3 c.c. the conversion was partial, nonlinear but still more than that corresponding to the break point, i.e., 3 cc., which is obviously the maximum capacity of 1.9048 g. of chromosorb-P nickel catalyst without leaving any unconverted reactant.

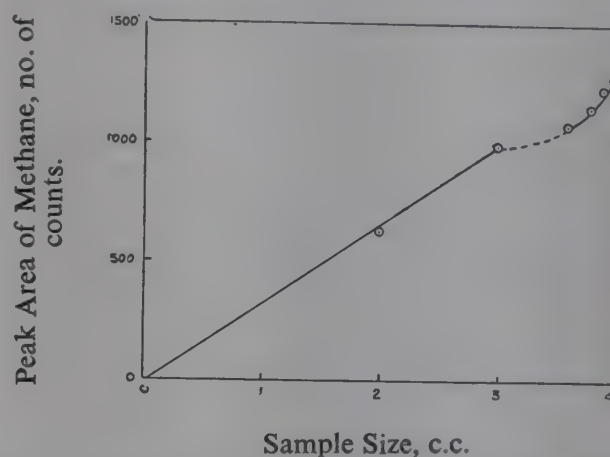


Fig. 4—Plot of the Peak Area of Converted Methane against the Sample Size in the Column Set-up.
[Porapak T 5' + Catalyst 5' + Porapak T 9']

Had the active sites on the catalyst been homogenous, the peak area of methane should remain constant at the break point. The non-linear portion, obviously testifies to the presence of heterogenous sites with different activation energies. The first kind of sites which are most active are responsible for the straightline portion of Fig. 4 and the other sites, which remained potential so long, began functioning and causing increased conversion leading to the nonlinear rise in methane peak area. The exact mechanism for the increase in the yield with larger sample sizes beyond 3 c.c. is unclear and awaits further study. One probable cause for non-linear increase in product beyond 3 c.c. may be the increase in space velocity of the reactant pulse giving lower contact time with the second kind of less active sites (the priority ones being fully engaged) giving increased amounts of unconverted carbon dioxide.

Suggested Applications

1. The GC method proposed for the prediction of catalytic activity should be extended to other cataly-

tic reactions on porous solids with a view to determine general rules about the nature of plots of Fig. 1B. Heterogenous catalysis is associated with chemisorption or activated adsorption, whereas a true GSC is limited to completely reversible physisorption forces. Obviously, the onset of catalysis on a porous solid must be reflected on one or more of the parameters of GSC elution, the break in the linearity of $\log V_g$ vs $1/T$ being most probable.

2. The exact location of the break point in Fig. 4 may be used for the computation of active surface area, assuming that the critical reactant size covers the active metal sites completely.

3. Although this study was made with the reactant carbon dioxide only, the same observations and conclusions will definitely be valid when carbon-monoxide is used.

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This paper deals with desulphurization of petroleum feedstock using alkalized iron oxide of different composition prepared in this laboratory. Synthetic solutions of organic sulphur compounds were prepared using known organic sulphur compounds, like ethyl mercaptan, carbon disulphide and thiophene, and their removal over alkalized iron oxide was studied under atmospheric pressure at 300°C.

Desulphurization of Petroleum Feedstocks Using Alkalized Iron Oxide

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The rapid growth of industries based on petroleum feedstocks has necessitated the availability of relatively sulphur-free products for further processing. Literature reveals that considerable use has been made and is still made of extraction, chemical processing and non-hydrocatalytic treatment of various petroleum fractions for sulphur removal or conversion of sulphur compounds to less objectionable end-products¹⁻³. However, hydrodesulphurization is the only method generally applicable for removal of all types of sulphur compounds.

Petroleum feedstocks are always associated with different types of organic sulphur compounds, like carbon disulphide, mercaptan, thiophene, etc. in varying quantities⁴. In the purification process for hydrodesulphurization in commercial operations, cobalt-molybdate catalyst is being most commonly used. The Ingredients of this catalyst are, however, not indigenously available and hence an attempt has been made to develop a catalyst based on an indigenous raw material. Such a catalyst may be an alkalized iron oxide, which has been used in Germany⁵ for removal of organic sulphur compounds from synthesis gas. The available information about its use is insufficient⁶.

This paper deals with the study of desulphurization of synthetic solutions of heptane with each one of the sulphur-bearing organic compounds, viz. carbon disulphide, ethyl mercaptan and thiophene of mol. wt. 100 and having C/H ratio 5.25, which has been chosen

since they resemble light petroleum naphtha in most of their physico-chemical properties.

Experimental

Apparatus : The experimental set-up (Fig. 1) comprised the following : (a) Electrically heated stainless steel (Type 321) preheater-cum-vaporizer tube each 25 mm. i.d. and 600 mm. long with a thermocouple well at the outlet end ; (b) one water-cooled copper-coil condenser ; (c) condensate receiver made of

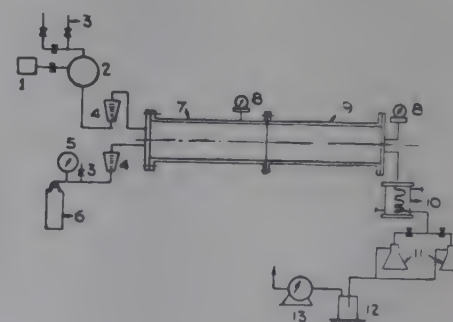


Fig. 1—Flow Diagram of Desulphurization Unit
Legend

- | | |
|------------------------------------|---|
| 1. Storage for Heptane solution | 2. Heptane feed vessel |
| 3. By-pass Regulator | 4. Rotameter |
| 5. Press-Gauge | 6. Hydrogen Cylinder |
| 7. Preheater (electrically heated) | 8. Millivoltmeter |
| 9. Reactor (electrically-heated) | 10. Condenser |
| 11. Condensate Receiver | 12. Absorption Vessel (Cd-Acetate solution) |
| 13. Wet Gasmeter | |

glass ; (d) one rotameter to measure the flow of liquid heptane ; (e) one rotameter for measuring the hydrogen flow. Before setting up the apparatus, the pre-

heater and reactor tubes were packed with 6 mm. alundum balls and in-between the balls a layer of alkalized iron oxide catalyst of a known weight and size was placed.

Materials Used : 1. Heptane—commercially pure, sp. gr. 0.718, boiling range 93 to 94°C ; contains olefines 5.5 per cent, aromatics 6.5 per cent, sulphur nil.

2. Carbon disulphide—chemically pure, molecular wt. 76.14, wt/c.c. at 20°C 1.262-1.267 g., boiling range (95 per cent) 45-47°C.

3. Ethyl mercaptan—chemically pure, molecular wt. 62.13, wt/c.c. at 20°C 0.835-0.838 g., boiling range (5 per cent) 34-36°C.

4. Thiophene—chemically pure, molecular wt. 84.14, wt/c.c. at 20°C 1.062-1.065 g., boiling range (95 per cent) 83-86°C.

5. Iron oxide catalyst containing 5, 10, 15 and 20 per cent alkali as sodium carbonate prepared in laboratory, size 6 mm. diam. and 6 mm. long.

6. Hydrogen—pure obtained from hydrogen cylinder.

Procedure : After assembling the apparatus, the pre-heater was heated to 150 to 200°C and the temperature of the reactor was maintained at the desired condition. The heptane solution of the individual organic sulphur compound was then introduced separately with simultaneous adjustment of condensate cooling water. The heptane solution and hydrogen rates were then adjusted to the desired values. The non-condensable gases were then metered by a wet gasometer, after passing through a cadmium acetate solution. Data were collected under a steady condition with different flow rates of hydrogen and heptane. Quantitative estimation of the sulphur compounds was done by the A.S.T.M. methods.

Results and Discussion

Table 1 shows the data of the experiments carried out with a series of alkalized iron oxide of different composition and it has been observed that an alkalized iron oxide of a suitable composition can be used for the removal of carbon disulphide and mercaptan-type of organic sulphur compounds but it is completely unsuitable for the thiophenic-type sulphur compounds most probably due to the latter's cyclic

Table 1—EXPERIMENTAL RESULTS: SYNTHETIC SOLUTIONS OF ORGANIC SULPHUR COMPOUNDS LIKE ETHYL MERCAPTAN AND CARBON DISULPHIDE IN HEPTANE
[Temperature of the Reactor 300°C; Wt. of Catalyst used 50 g.]

Sl. No.	Catalyst Composition	FHC, g. Moles of hydrogen/hr in Feed	FHC, g. Moles of Heptane/hr in Feed	F. Total Feed, g. Moles/hr	Sulphur Content in Heptane Feed, ppm wt./wt.	Sulphur Content in Heptane Product, ppm wt./wt.	Cumulative Retention of Sulphur, g.	Percentage Removal of Sulphur
1	2	3	4	5	6	7	8	9
A : With Ethyl Mercaptan								
1.	Iron Oxide pure	0.95	0.44	1.39	466.2	Nil	0.17	100.0
2.	"	0.95	0.48	1.43	466.2	1.6	0.39	96.4
3.	"	0.94	0.50	1.44	466.0	9.4	0.599	98.0
4.	"	0.82	0.55	1.37	466.0	12.0	0.710	97.4
5.	"	0.91	0.55	1.46	460.0	26.7	0.82	94.2
1.	5% alkalized iron oxide	1.07	0.56	1.63	608.0	Nil	0.9	100.0
2.	"	0.71	0.52	1.23	608.0	8.5	0.40	98.6
3.	"	0.80	0.60	1.40	608.0	27.5	0.75	95.5
4.	"	1.0	0.55	1.55	608.0	8.5	1.08	98.6
5.	"	1.0	0.55	1.55	608.0	8.5	1.41	98.6
6.	"	0.89	0.55	1.44	608.0	19.4	1.72	98.8
7.	"	0.94	0.52	1.46	625.0	12.3	2.03	96.2
8.	"	1.10	0.49	1.59	625.0	38.7	2.11	93.8
9.	"	0.96	0.52	1.48	625.0	60.0	2.43	90.4
10.	"	0.81	0.50	1.31	600.0	90.0	3.0	85.0
1.	10% alkalized iron oxide	0.75	0.67	1.42	510.0	Nil	0.48	100.0
2.	"	0.83	0.54	1.37	707.0	Nil	0.69	100.0
3.	"	0.76	0.60	1.36	1120.0	26.7	1.18	97.6
4.	"	0.73	0.60	1.33	1430.0	100.8	2.01	91.6
5.	"	0.86	0.42	1.28	1430.0	208.5	2.57	85.4
6.	"	0.77	0.55	1.32	1500.0	286.0	3.66	80.0
7.	"	0.74	0.53	1.27	1500.0	369.0	4.01	75.4

Table 1—EXPERIMENTAL RESULTS: SYNTHETIC SOLUTIONS OF ORGANIC SULPHUR COMPOUNDS LIKE ETHYL MERCAPTAN AND CARBON DISULPHIDE IN HEPTANE (Contd.)

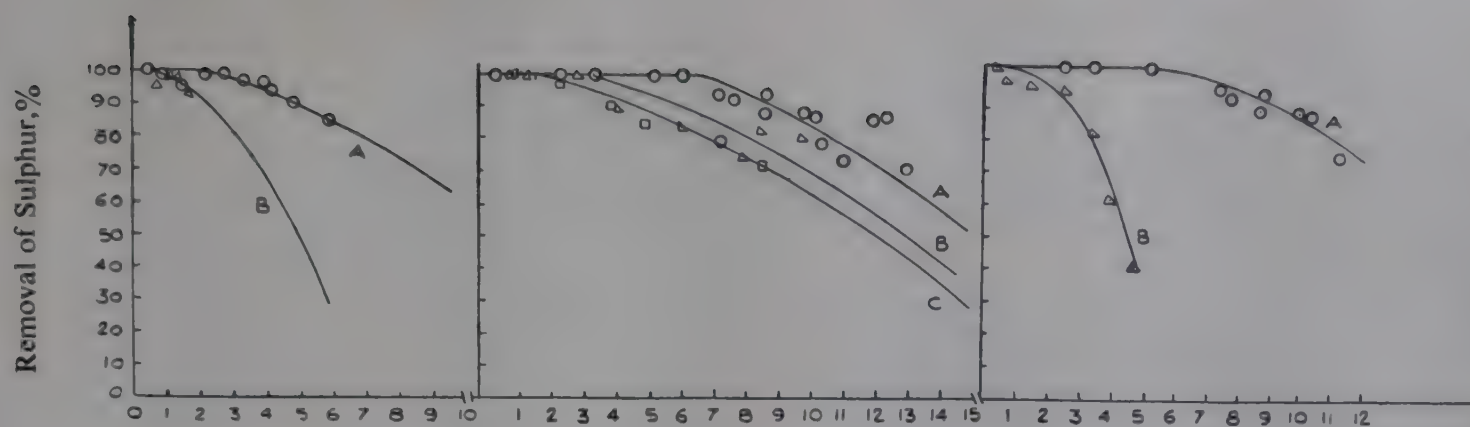
[Temperature of the Reactor 300°C; Wt. of Catalyst used 50 g.]

Sl. No.	Catalyst Composition	FHC, g. Moles of hydrogen hr in Feed	FHC, g. Moles of Heptane/hr in Feed	F. Total Feed, g. Moles/hr	Sulphur Content in Heptane Feed, ppm wt./wt.	Sulphur Content in Heptane Product, ppm wt./wt.	Cumulative Retention of Sulphur, g.	Percentage Removal of Sulphur
1	2	3	4	5	6	7	8	9
1.	15% alkalized iron oxide	1.1	0.25	1.35	200.0	Nil	0.182	100
2.	"	1.3	1.64	1.64	606.0	Nil	0.426	100
3.	"	1.10	1.44	1.44	717.0	Nil	0.715	100
4.	"	1.0	1.38	1.38	3250.0	Nil	1.45	100
5.	"	1.2	1.58	1.58	3250.0	340	2.11	89.8
6.	"	1.1	1.39	1.39	3250.0	500	3.08	84.6
7.	"	1.1	1.31	1.31	717.0	170	3.98	76.3
8.	"	1.1	1.31	1.31	1140.0	182	4.34	83.3
9.	"	1.1	1.44	1.44	2016.0	390	4.997	80.6
10.	"	0.96	1.00	1.30	1550.0	320	5.24	79.3
1.	20% alkalized iron oxide	0.97	0.67	1.64	980.0	Nil	0.214	100
2.	"	1.0	0.67	1.67	1115.0	Nil	0.808	100
3.	"	1.2	0.59	1.81	970.0	Nil	1.21	100
4.	"	1.1	0.55	1.65	1229.0	Nil	1.75	100
5.	"	1.1	0.59	1.69	1190.0	Nil	2.65	100
6.	"	1.0	0.67	1.67	941.0	Nil	3.087	100
7.	"	1.1	0.67	1.77	826.0	48.0	3.66	94.2
8.	"	1.1	0.46	1.56	886.0	67.6	3.908	92.3
9.	"	1.1	0.59	1.69	749.5	86.8	4.353	88.4
10.	"	1.1	0.50	1.60	749.5	49.0	4.423	93.5
11.	"	1.1	0.42	1.52	1037.0	125.0	4.959	88.0
12.	"	0.77	0.4	1.17	1115.0	144.0	5.204	87.1
13.	"	1.0	0.59	1.59	1096.0	288.0	5.61	73.6
14.	"	1.3	0.42	1.72	923.0	127.0	6.03	86.2
15.	"	1.1	0.63	1.73	702.0	90.0	6.26	87.2
16.	"	1.0	0.63	1.63	702.0	200.0	6.51	71.5
B : Carbon disulphide								
1.	Iron oxide pure	1.07	0.52	1.59	360	8.3	0.1	97.2
2.	"	1.07	0.50	1.57	360	8.2	0.6	97.4
3.	"	0.91	0.53	1.44	351	8.1	1.1	97.7
4.	"	0.90	0.53	1.43	351	7.7	1.3	97.8
5.	"	0.90	0.57	1.47	413	11.1	2.3	97.3
6.	"	0.90	0.53	1.43	413	9.5	3.5	97.7
7.	"	1.0	0.50	1.50	413	24.4	3.7	94.1
8.	"	0.9	0.50	1.10	537	20.9	3.9	96.1
9.	"	0.8	0.57	1.37	537	36.0	4.6	93.3
10.	"	0.98	0.78	1.76	483	48.2	5.2	90.0
11.	"	0.98	0.69	1.67	483	67.6	5.4	86.0
12.	"	0.95	0.65	1.60	537	107.4	6.2	80.0
1.	5% alkalized iron oxide	0.86	0.81	1.67	633.6	Nil	0.513	100
2.	"	0.75	0.63	1.38	633.6	Nil	0.672	100
3.	"	0.92	0.62	1.54	633.6	Nil	0.897	100
4.	"	0.76	0.56	1.32	588.3	11.8	1.120	98
5.	"	0.83	0.56	1.39	543.1	21.7	1.394	96
6.	"	0.71	0.67	1.38	543.1	21.7	1.512	96
7.	"	0.76	0.54	1.30	588.3	23.5	1.787	96.0
8.	"	0.74	0.45	1.19	478.7	26.8	2.054	94.4
9.	"	0.73	0.42	1.15	478.7	36.9	2.463	92.3
10.	"	0.85	0.56	1.41	406.7	48.8	3.004	88.0
11.	"	0.86	0.60	1.46	387.0	55.4	3.695	85.7
12.	"	0.77	0.58	1.35	387.0	89.0	4.003	77.0
13.	"	0.60	0.54	1.14	437.9	101.8	4.261	76.7
14.	"	0.80	0.48	1.28	437.9	108.1	4.562	75.3
15.	"	0.76	0.56	1.32	407.4	99.3	4.785	75.8
16.	"	0.78	0.42	1.20	397.2	118.2	5.131	70.4
17.	"	0.74	0.56	1.30	397.2	134.7	5.398	66.1
18.	"	0.89	0.55	1.44	366.7	124.8	5.684	66.0
19.	"	0.70	0.53	1.23	478.7	196.8	6.234	58.9
20.	"	0.78	0.52	1.30	529.6	232.9	6.750	56.0
21.	"	0.80	0.64	1.44	529.6	258.3	7.071	51.2

Table 1—EXPERIMENTAL RESULTS: SYNTHETIC SOLUTIONS OF ORGANIC SULPHUR COMPOUNDS LIKE ETHYL MERCAPTAN AND CARBON DISULPHIDE IN HEPTANE (Contd.)

[Temperature of the Reactor 300°C; Wt. of Catalyst used 50 g.]

Sl. No.	Catalyst Composition	FHC, g. Moles of hydrogen/hr in Feed	FHC, g. Moles of Heptane/hr in Feed	F. Total Feed, g. Moles/hr	Sulphur Content in Heptane Feed, ppm wt./wt.	Sulphur Content in Heptane Product, ppm wt./wt.	Cumulative Retention of Sulphur, g.	Percentage Removal of Sulphur
1	2	3	4	5	6	7	8	9
1.	5% alkalized iron oxide regenerated	0.81	0.59	1.40	478.5	Nil	0.26	100
2.	"	0.81	0.66	1.47	468.3	Nil	0.506	100
3.	"	0.82	0.59	1.41	458.1	Nil	0.934	100
4.	"	1.02	0.55	1.57	447.9	23.6	1.267	46.8
5.	"	0.68	0.59	1.27	411.8	20.05	1.76	95.3
6.	"	0.78	0.63	1.41	365.4	21.1	2.31	94.2
7.	"	0.77	0.54	1.31	434.3	27.4	2.64	93.7
8.	"	0.77	0.57	1.34	464.8	46.5	3.125	90.0
9.	"	0.71	0.58	1.29	464.8	50.6	3.618	89.1
10.	"	0.75	0.42	1.17	395.2	58.5	3.900	85.2
11.	"	0.86	0.59	1.45	403.9	67.0	4.214	83.4
12.	"	0.79	0.57	1.36	403.9	76.7	5.09	81.0
13.	"	0.75	0.63	1.38	480.1	98.9	5.695	79.0
14.	"	0.70	0.55	1.25	502.9	140.8	6.26	72.0
1.	10% alkalized iron oxide	0.81	0.50	1.31	610.0	Nil	0.8	100
2.	"	0.68	0.34	1.02	610.0	22.0	1.1	96.4
3.	"	0.77	0.38	1.15	580.2	36.5	1.6	93.7
4.	"	0.71	0.50	1.21	580.2	58.0	2.0	90.0
5.	"	1.0	0.46	1.46	541.0	79.9	2.3	85.2
6.	"	0.8	0.50	1.30	541.0	96.7	2.7	82.1
7.	"	0.83	0.42	1.25	578.0	126.0	3.1	78.2
8.	"	0.73	0.42	1.15	500.0	134.5	3.5	73.1
9.	"	0.86	0.34	1.20	510.0	151.5	3.7	70.3
10.	"	0.77	0.50	1.27	510.0	178.5	4.1	65.0
1.	15% alkalized iron oxide	0.50	0.58	1.38	329.3	Nil	0.274	100
2.	"	0.75	0.69	1.44	329.3	10.9	0.409	96.7
3.	"	0.64	0.49	1.13	600.0	9.6	0.55	98.4
4.	"	0.81	0.48	1.29	600.0	12.0	0.68	98.0
5.	"	0.78	0.60	1.38	587.2	23.5	1.23	96.0
6.	"	0.68	0.60	1.28	531.6	50.9	1.51	90.4
7.	"	0.72	0.62	1.34	555.4	113.3	2.05	79.6
8.	"	0.77	0.67	1.44	547.1	147.8	2.60	73.0
9.	"	0.75	0.57	1.92	547.1	191.5	2.97	64.97
10.	"	0.77	0.55	1.32	542.7	217.1	3.47	60.0
1.	20% alkalized iron oxide	0.81	0.61	1.42	609.6	Nil	0.18	100
2.	"	0.77	0.53	1.30	609.6	Nil	0.50	100
3.	"	0.80	0.55	1.35	609.6	34.1	0.8	94.4
4.	"	0.74	0.58	1.32	602.0	93.9	1.4	84.6
5.	"	0.75	0.55	1.30	617.2	138.6	1.8	79.10
6.	"	0.77	0.68	1.45	579.1	124.0	2.02	78.6
7.	"	0.72	0.45	1.17	533.4	155.7	2.37	70.8
8.	"	0.69	0.57	1.26	541.0	165.7	2.6	69.0
9.	"	0.70	0.57	1.27	563.9	236.2	3.0	58.1
10.	"	0.70	0.55	1.25	594.4	256.8	3.4	55.8
1.	20% alkalized iron oxide regenerated	0.75	0.53	1.31	594.4	Nil	0.3	100.0
2.	"	0.85	0.53	1.38	594.4	16.6	0.5	97.2
3.	"	0.78	0.55	1.33	670.6	33.5	0.9	95.0
4.	"	0.65	0.64	1.29	468.6	50.1	1.6	89.3
5.	"	0.76	0.60	1.36	468.6	102.6	1.75	87.1
6.	"	0.77	0.53	1.30	571.5	140.2	2.4	80.0
7.	"	0.74	0.55	1.29	658.8	184.5	2.6	72.0



Retention of Sulphur, g./100 g. Cat.

Retention of Sulphur, g./100 g. Cat.

Retention of Sulphur, g./100 g. Cat.

Fig. 2—Retention Vs. Per cent Removal of Sulphur with Mercaptan

A—50g. Catalyst containing 5% Alkali, Feed Heptane Soln. containing 300—600 ppm, 60—108 cc. Liq./hr; Hydrogen Rate 9—15 l./hr; Temp. 300°C; Pressure: Atm.

B—50g. Catalyst containing no alkali, other conditions same as A.

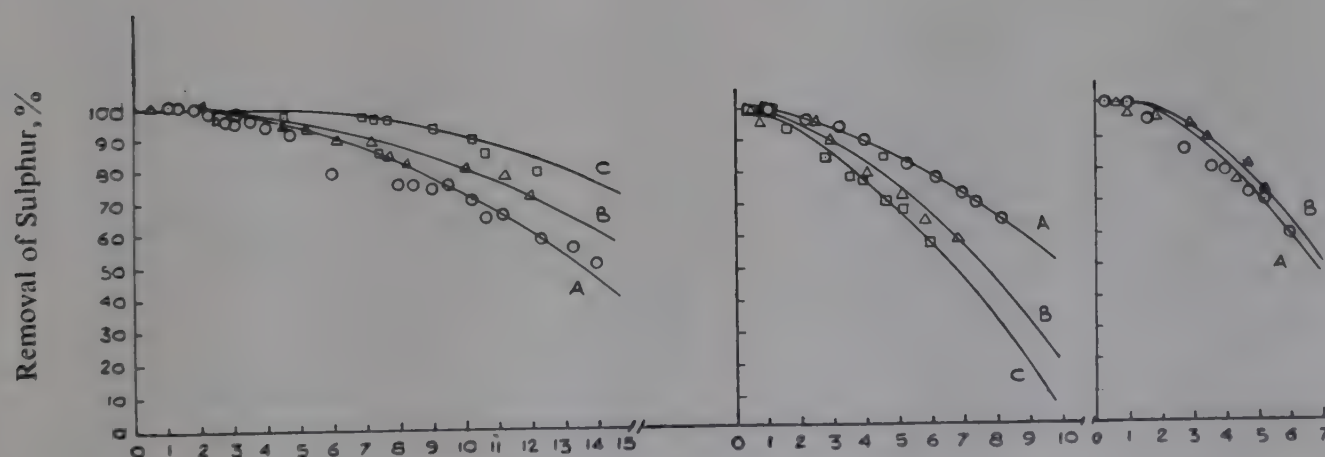
A—50g. Catalyst containing 20% Alkali, Feed Heptane soln. containing 700—1230 ppm 30—72 cc. liq./hr; hydrogen rate 9—15 l./hr; Temp. 300°C; Pressure: Atm.

B—50g. Catalyst containing 15% Alkali, Feed Heptane soln. containing 200—3250 ppm; 30—150 cc. liq./hr; Hydrogen rate 6—15 l./hr; Temp. 300°C; Pressure: Atm.

C—50g. Catalyst containing 10% Alkali, Feed Heptane soln. containing 700—1500 ppm, 60—100 cc. Liq./hr. Hydrogen rate 8—10 l./hr. Temp. 300°C Pressure Atm.

A—50g. Catalyst containing 20% Alkali, Feed Heptane soln. containing 700—1230 ppm 30—72 cc. liq./hr; Hydrogen rate 9—1.5 l./hr; Temp. 300°C; Pressure: Atm.

B—Same as A after regeneration with steam at 450°C.



Retention of Sulphur, g./100g. Cat.

Retention of Sulphur, g./100g. Cat.

Retention of Sulphur, g./100g. Cat.

Fig. 3—Retention Vs. Per cent Removal of Sulphur with Carbon Disulphide

A—50g. Catalyst containing 5% Alkali, Feed Heptane Solution 350—650 ppm 60—120 cc. liq./hr; Hydrogen rate 7—10 l./hr; Temp., 300°C; Pressure: Atm.

B—Same as A after regeneration with steam at 45°C.

C—50g. Catalyst containing no Alkali, other conditions same as A.

A—50g. Catalyst containing 10% Alkali, Feed Heptane Solution 500—610 ppm. 30—120 cc. liq./hr; Hydrogen rate 11 l./hr. Temp. 300°C; Pressure: Atm.

B—50g. Catalyst containing 15% Alkali, Feed Heptane Solution containing 325—600 ppm. 30—130 cc. liq./hr; Hydrogen rate 9—12 l./hr; Temp. 300°C; Pressure: Atm.

C—50g. Catalyst containing 20% Alkali, Feed Heptane soln. containing 500—600 ppm. 30—114 cc. liq./hr; Hydrogen rate 6—11 l./hr; Temp. 300°C; Pressure: Atm.

A—50g. Catalyst containing 20 Alkali, Feed Heptane soln. containing 500—600 ppm. 30—114 cc. liq./hr; Hydrogen rate 6—11 l./hr; Temp. 300°C; Pressure: Atm.

B—Same as A after regeneration with steam at 450°C.

structure. The latter may, however, be removed either by adsorption with active carbon or an activated acid treatment operation. An activated acid refining process has been developed which is highly effective in the removal of thiophenic and mercaptan-type sulphur compounds but it is inactive with carbon disulphide.

From the experimental data (Table 1) it has been found that for removal of carbon disulphide, an alkalized iron oxide of low alkali content is preferable whereas for removal of mercaptan sulphur, higher alkali content is preferred. The spent alkalized iron oxide can also be regenerated easily by simply steaming around 450°C. The regenerated alkalized iron oxide shows improved activity in the case of carbon disulphide (Fig. 2) whereas its activity gradually decreases with mercaptans.

Chemical analysis for the alkali content in the original and regenerated samples of alkalized iron oxide were carried out, which revealed that a lowering of the alkali content takes place due to the fact that regeneration has a lowering effect on the alkalinity of the alkalized iron oxide and hence a regenerated alkalized iron oxide shows an improved activity in case of carbon disulphide-type sulphur compounds but in the case of mercaptans the result is the reverse. Table 1 gives the experimental data with pure iron oxide catalyst prepared in the laboratory and it is found that pure iron oxide catalyst can remove carbon disulphide-type compounds better in comparison to alkalized iron oxide whereas mercaptans are removed with higher alkali content and hence a compromise has to be made for the alkali content for removal of disulphide and mercaptans (Experimental data have been plotted in Fig. 2).

Work on optimization is in progress which will be published in a subsequent paper. This work has been undertaken for studying steam-hydrocarbon reforming for the production of synthesis gas. At present the feedstocks for synthesis gas production by the steam-reforming process ranges from natural gas (essentially methane together with a few per cent higher boiling hydrocarbon) and light petroleum gasoline (mainly butane with some butene and higher boiling hydrocarbons) to light distillate fractions in the boiling range 40-170°C. The type and concentration of sulphur compounds present in these feedstocks

depend on the latter's boiling range and the source. Natural gas contains mainly hydrogen sulphide and low boiling sulphides or mercaptans while light petroleum gasoline contains similar compounds with higher boiling range and the light distillates contain a large range of compounds of different types. Desulphurization of the first two feedstocks can be done very easily by alkalized iron oxide alone, whereas for light distillate fraction desulphurization with alkalized iron oxide together with a prior refining with activated acid may be a suitable substitute for cobalt molybdate catalyst.

These laboratory experiments were carried out with H_2 : naphtha ratio varying from approximately 0.3 to 2.8 moles/mole and thus a hydro desulphurization unit has been operated under the partial pressure of hydrogen between 0.4 and 0.8 ata. Hydrodesulphurization of naphtha under commercial conditions is usually done under pressure, with a H_2 /naphtha ratio of 0.2 and 1.0 and a partial pressure of hydrogen between 2 and 10 ata. Since the laboratory unit was operated under atmospheric pressure, the present experiment was done under a lower partial pressure of hydrogen than a commercial plant and so we have operated under higher H_2 /naphtha ratio so as to obtain an appreciable conversion.

Nomenclature

F_{HC} = g. moles hydrocarbon/hr

F_H = g. moles hydrogen/hr

F = total feed g. moles (hydrogen + hydrocarbon)/hr

W_R = Wt. of catalyst, g.

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Utilization of Process Waste in Catalyst Production: A Method of Recovery of Catalyst Material

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Catalyst materials, like nickel, copper and zinc, have been recovered from the effluent of a catalyst manufacturing process by breaking the metal amino complexes formed during the process. This method has been developed by considering the instability constant of the complex at an elevated temperature along with the effect of dilution of the metal amino complexes under some optimum conditions. There is no capital investment and the proposed method is simple compared to all conventional procedures. The recovery of metals is encouraging.

The metals used as catalyst are not in plenty in India, and the scarcity in some of them are posing problems for their manufacture. This has led many scientists to search for the possible sources of these metals or to establish a convenient method for their recovery from the available effluent.

Among the methods for the recovery of the metals, the destruction of amino complexes of the metal present in the effluents is normally done by treating the latter with a suitable chemical agent. This process has attracted the attention of the scientists and technologists from a long time. A few workers²⁻⁴ have reported recovery of nickel from the effluents and some patents are also available. A number of workers⁵⁻¹¹ have made investigation on the recovery of copper and zinc from effluents and other possible sources.

In the present study, an attempt has been made successfully to decompose the amino complexes by considering their susceptibility to the environmental conditions, as well as to the concentration factor of the complexes.

Theory

Most of the metal amino complexes are liable in nature



where x is the oxidation number of metal ion M and y is the coordination number of M^{+x} . They are

decomposed by chemical or thermal treatment. However, it is worthwhile mentioning that the presence of excess ammonium salts in effluents causes great problem to extract the metal by a common method. It is well-known that transitional elements have the affinity to form amino complexes, where an excess ammonium salts are available in the reacting system. These amino complexes are present in a number of effluents of industrial processes.

EXPERIMENTAL & DISCUSSION

Destruction of Metal Amino Complex

The main difficulty lies in the alkali digestion technique by presence of a large amount of ammonium salts in the effluents which require considerable amount of the reagents. The contamination of alkali in the precipitated mass, which has to be removed by thorough washing, poses another problem.

Organic reagents may be applied for extraction but are uneconomical due to high price of the chemicals. In some cases, by using a cheaper organic acid as precipitant or by adopting a suitable solvent, extraction can be carried out.

Ion-exchange methods are also used in certain cases where concentration of the metal in the effluent is very low. These method are not applicable for higher concentration of metal. The direct electrolysis has also been discarded as it is uneconomical and inconvenient in practice. Keeping all these points in view, a method has been developed by considering

the instability constant of the complex at elevated temperature and the effect of dilution on the metal amino complexes, simultaneously under some optimum conditions for their decomposition.

Effect of Dilution and Temperature

The change in the concentration of the amino complexes in the effluent and the temperature factor can be applied simultaneously just adding the complexes to an excess boiled water.

The significant aspects of the recovery process are (i) the efficiency of the dilution is fully utilized by adding the amino complexes slowly to an excess water and not *Vice Versa*, and (ii) large number of water molecules are available for attacking the complex ions and replace the coordinated ammonia molecules from the $M(NH_3)_y^+ x$ ion. The concentration of amino complexes as well as the concentration of ammonium salts in the effluents change all on a sudden causing thereby the destruction of the complexes. The pH of the effluent is not affected very much during dilution; it remains in the range 7.5 to 8.5.

Recovery of Nickel, Copper and Zinc from Amino Complexes

(1) *Nickel*: During manufacture of alumina-based nickel reformation catalyst, incomplete precipitation in the process causes loss of nickel in the effluent. For this reason, a slight excess of precipitating agent is always recommended for complete precipitation. The addition of slight excess of precipitating agent for complete precipitation helps the formation of the amino complex to some extent, which comes out with the effluent.

The soluble nickel amino complexes expected to be formed in the effluent during the precipitation reaction may be as follows: (i) $[Ni(NH_3)_6-] CO_3, NH_4(NO_3)$ (Aq); (ii) $[Ni(NH_3)_5[(H_2O)] CO_3, NH_4(NO_3)$ (Aq); and (iii) $[Ni(NH_3)_4(H_2O)_2](NO_3)_2, NH_4(NO_3)$ (Aq) They all come out in the form of a greenish solution having pH=8.0-8.5 and is drained out as effluent. The composition of the system depends upon the plant process and composition of reacting solutions. The presence of free acids in the reacting solutions, which form ammonium salts in greater proportion, increases the tendency of complex formation of the metal ion. The addition of excess precipitating agent forms the complex and the extent of complex formation depends on the amount of excess reagent. The general composition of the industrial effluents from

the nickel reformation catalyst plant varies from sample to sample.

For the present investigation, an effluent having the following composition (per cent by weight) was studied by both dilution and digestion with caustic soda techniques: nickel 2.00, ammoniacal nitrogen 6.4; nitrate nitrogen 6.0; rest water.

The recovery of nickel is best possible by maintaining a higher dilution ratio (amino complex: water: 1: 30). As nickel amino complex is fairly stable at room temperature and even on boiling, the complete recovery of nickel is difficult if the above dilution is not maintained. But the dilution efficiency is dependent on the amount of ammonium salt present.

TABLE 1—COMPARATIVE RESULTS OF NICKEL—RECOVERY FROM EFFLUENTS

1. Source: Effluents Containing Nickel Amino-Complexes
2. Quantity of Charge: 1 lit.
3. Colour: green
4. pH: 8.5
5. Analysis of Effluent: (%)· Ni 2.0, Nitrate N 6.0 and Ammoniacal N 6.4

	Digestion Technique	Dilution Technique
1.(a) Stoichiometric requirement of caustic soda (flakes) based on chemical analysis, g.	172	Nil
(b) Actual requirement of caustic soda flakes, g.	180	—
2. Reaction temperature, °C	100-110	100-110
3. Time of digestion, hr	2	1
4. Heating device	Steam heating	Steam heating
5. Amount of nitric acid required for digestion, ml.	70	70
6. Total yield of crystalline nickel nitrate, g.	91	92
7. Yield, %	93-95	94-95

TABLE 2—RECOVERIES OF NICKEL, COPPER AND ZINC FROM EFFLUENTS

Sl. No.	Nickel Content in the Effluent, % by wt.	Nickel Re-covered, %	Sl. No.	Copper Content in the Effluent, % by wt.	Copper Re-covered, %	Sl. No.	Zinc Content in the Effluent, % by wt.	Zinc Re-covered, %
I	1.83	94.28	I	1.82	94.81	I	2.20	94.25
II	2.04	94.41	II	2.15	93.65	II	1.85	94.62
III	2.42	93.26	III	1.66	95.20	III	1.62	93.80

In this process, the effluent is added to water in the ratio mentioned above with continuous stirring for 1 hr. at the boiling temperature. It is then allowed to settle and filtered. The precipitated mass is thoroughly washed with condensed water. The

thoroughly washed greenish white fine precipitate of nickel hydroxide is then dissolved in 40 per cent (W/V) nitric acid to make a crude liquor of nickel nitrate solution. The liquor is crystallized further to obtain a product having phase composition nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ as identified by x-ray study.

(2) *Copper*: The mother effluents containing copper amino-complexes are available from different industrial wastes. The Cu^{2+} ion follows more or less the same pattern in complex formation with ammonia molecule, when precipitating agent is added in slight excess for complete precipitation.

The same principle, as applied in the case of recovery of nickel, has also been used for the recovery of copper. In case of copper amino complexes decomposition is easier. The composition of effluent is dependent on the reaction condition and plant operation. An effluent having the following composition (per cent by weight) was studied for the recovery process: copper 1.66 ammoniacal nitrogen 4.8; free ammonia negligible and rest water.

TABLE 3—RESULTS OF COPPER RECOVERY FROM EFFLUENTS

1. Source: Effluents Containing Copper-amino complex
2. Quantity of Charge: 1 lit.;
3. pH: 8.5
4. Colour: blue
5. Analysis of effluents (%): Copper 1.66; Ammoniacal nitrogen 4.8; free ammonia: negligible
5. Volume of boiled water taken: 20 lit.
7. Reaction temperature: 100-110°C;
8. Digestion period: 30 min.
9. Amount of nitric acid (48%) required for digestion—50 ml.
10. Heating device: Steam heating
11. Total yield of crystalline copper nitrate 61 g.
12. Yield 95-96%

The complete recovery is done by adding 1 litre of the effluent mother liquor to 20 lit. of condensed water heated to 100°C with constant stirring and then further boiling for 30 min. At first hydroxide is precipitated but hydrated oxide is transformed gradually into oxide on heating. The addition is done slowly with constant stirring to increase the efficiency of the recovery process. The precipitated mass is dissolved in commercial nitric acid to make crude liquor of copper nitrate solution. The crude copper nitrate solution liquor is crystallized further to yield a product having phase composition $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as identified by x-ray observation.

(3) *Zinc*: Zn^{2+} follows the same pattern of complex formation as Cu^{2+} during precipitation with excess reagent and recovery can also be made successfully. The same principle is also applicable for the recovery of zinc. The effluents was studied having the composition (per cent by weight): zinc 2.2 ammoniacal nitrogen 5.4 and free ammonia negligible. The recovery of zinc has been done by maintaining the following dilution ratio and boiling the diluted mixture 1 hr with constant stirring (amino complex: Water : : 1:25). In this case, the precipitated mass is treated with nitric acid to get crystallized

TABLE 4—RESULTS OF ZINC RECOVERY FROM EFFLUENTS

1. Source: Effluent Containing Zinc-amino complex
2. Quantity of charge: 1 lit. ;
3. Colour: colourless;
4. pH 8.5;
5. Analysis of Effluents (%): Zn 2.2 Ammoniacal N 5.4 and Free NH_3 negligible
6. Volume of boiled water taken: 25 lit.
7. Reaction temperature: 100-110°C;
8. Digestion Period: 1 hr.;
9. Amount of nitric acid (48%) required for digestion: 65 ml
10. Heating device: Steam heating;
11. Total yield of zinc nitrate: 94.6 g.;
12. Yield: 94-95%

TABLE 5—RECOVERY OF NICKEL, COPPER AND ZINC WITH DILUTION

Sl. No.	Dilution Ratio of Volume of Effluent to Volume of Water	% Recovery of Nickel (Nickel content 2.0% by wt.)	% Recovery of Copper (Copper Content 1.66% by wt.)	% Recovery of Zinc (Zinc Content 2.2% by wt.)
1.	1 5	28.20	51.41	43.24
2.	1:10	41.25	64.52	58.15
3.	1:15	60.82	82.20	78.12
4.	1 20	72.45	95.42	90.23
5.	1 25	85.28	95.60	94.15
6.	1 30	94.61	95.51	94.34

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as identified by x-ray observation. It should be mentioned here that if the waste mother liquor contains different metal-amino complexes then the precipitated product will be a mixture of respective metal oxides or hydroxides. The individual separation is generally not essential for reusing the recovered product in the same plant. Also no such individual separation reported from a waste mother liquor containing different metal amino complexes.

Conclusion

It has been observed from the result of percentage yield of nickel, copper and zinc that the dilution tech-

nique applied to the process effluent can be well compared with other methods like precipitation technique as carbonates or as hydroxide. In the case of carbonates, it has been found that the reaction is slow and precipitation remains incomplete. In the other method of precipitation as hydroxide the disadvantage of losing the metal at the time of washing, is very much prominent. Some of the salient advantages of the present method are (i) the recovery process adopted requires no capital investment and is suitable for a small capacity unit. (ii) The recovered product will be free from any contamination of foreign materials as no chemicals is required in this process. There may be a slight contamination of ammonium nitrate which is not objectionable. (iii) If the recovery is done by other methods say alkali treatment—the washing becomes a problem to make the product alkali free. In the present process, washing is not a problem.

Since the use of nickel, copper and zinc as catalysts is rapidly increasing in fertilizer, petrochemical and allied industries, the recovery of the above metals from process wastes and effluents should be given priority.

Acknowledgements

The authors' thanks are due to Dr. B. K. Banerjee, Superintendent for his keen interest, to Dr. S. K. Ghosh, Deputy Superintendent, for many valuable suggestions during the progress of this work and lastly to Sri K. B. Deb, Asstt. Project Engineer, for helpful discussion.

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The electric dipole moment of all the three isomers of anisidines and toluidines are determined in dilute benzene solution at 35°C. The theoretical values are calculated using Eyring equation. It is noted that observed values are in better agreement with the calculated values for which the induced effects have been taken into consideration. The extrapolated values of the gas phase dipole moment are also reported.

Dipole Moment of Some Disubstituted Anilines in Benzene Solution

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Introduction

The dipole moment of polar molecule in a non-polar solvent¹⁻⁴ allows the polar molecule to be studied in a quasi-isolated state. The molecular structure and the dipole moment values are closely related. The present paper reports the values of dipole moment for all three isomers of anisidines and toluidines (i.e. methoxy and methyl substituted anilines) in dilute benzene solution and the results have been discussed in the light of their molecular structure. These molecules seem particularly interesting because of an earlier reported correlation between their dipole moment and molecular association.⁵

Experimental

The AR grade chemicals *o*-, *p*-toluidines and *p*-anisidine were Riedel-make, while *o*-, *m*-anisidines *m*-toluidine were BDH-make. The AR grade benzene used in the solution work was supplied by BDH (India). All the chemicals were further purified thrice by fractional distillation before use. The physical properties of the chemicals used have been found to be in good agreement with the literature values.

The measurement of the static dielectric constant of all the substances in dilute benzene solution was done at 450 KHz by a Q-meter assembly as described earlier⁵⁻⁷. The temperature of the dielectric cell was maintained at 35°C by circulating water from a constant temperature bath through copper tubing coiled around the cell.

The dipole moment has been evaluated from the equation^{8, 9}:

$$\mu = \beta \left(\frac{d \epsilon_{012}}{d f_2} \right)^{\frac{1}{2}} \quad (1)$$

where μ represents the electrical dipole moment of the solute molecule, $\left(\frac{d \epsilon_{012}}{d f_2} \right)$ denotes the slope of the curve obtained by plotting the static dielectric constant of the solution (ϵ_{012}) against mole fraction (f_2) of the solute, β is a constant for the solvent [for benzene $\beta = 0.828 \times 10^{-18}$ esu]. The concentration of the solution has been kept low otherwise ϵ_{012} versus f_2 plot deviates from the straight lines behaviour as a result of dipole-dipole interaction effect at higher concentration.

Results and Discussion

The values of the dipole moment of all the six substances were evaluated using equation (1). The plot of the variation of static dielectric constant (ϵ_{012}) against mole fraction (f_2) for anisidines and toluidines are shown in Figs. 1 and 2 respectively. The dipole moment values are presented in Table 1 along with the theoretically calculated and literature values. The present values of dipole moment are in close agreement with the literature values. It can be seen (Table 1) that for different isomers of anisidines, the order of their dipole moment values are: *ortho* < *meta* < *para*. Such type of increase in dipole moment values has been observed in those of halotoluenes and haloethylbenzene by Murty,^{10, 11} in nitro-

TABLE 1—DIPOLE MOMENT OF ANISIDINES AND TOLUIDINES IN DEBYE UNITS

Substance	μ_{sol} Observed	Calculated Values of Dipole Moment			Extrapolated Values of Dipole Moment (μ_G) in Gas Phase		Literature* Values μ_{sol}
		A	B	C	D	E	
<i>o</i> -Anisidine	1.55	1.74	1.77	1.61	1.46	1.62	1.45-1.53
<i>m</i> -Anisidine	1.87	2.18	2.16	1.81	1.77	1.95	1.71-1.85
<i>p</i> -Anisidine	1.96	2.37	2.33	1.96	1.87	2.38	1.82-1.96
<i>o</i> -Toluidine	1.62	1.72	1.69	1.63	1.53	1.69	1.58-1.60
<i>m</i> -Toluidine	1.54	1.41	1.44	1.38	1.46	1.61	1.44-1.58
<i>p</i> -Toluidine	1.41	1.23	1.30	1.23	1.33	1.71	1.28-1.52

* Wesson, L. G., *Table of Electric Dipole Moments* (Technology Press, M.I.T. Cambridge, Mass). 1948.

- A— Values of dipole moment calculated by Eyring equation (2 taking para methyl compound as the basis in calculating the inclination of the group moment.
 B— Same as A but taking para chloro compound as the basis in calculating inclination of group moment.
 C— Calculated by Smallwood and Herzfeld method).
 D— Calculated using Guggenheim equation (3).
 E— Calculated using Higasi equation (4).

toluene by Devar and Paranjape¹² and in cresol by Mehrotra¹³ *et al.* Further, it can be seen from Table 1 that the values of dipole moment are in the decreasing order for the same sequence in the case of different isomers of toluidines, viz. *ortho* > *meta* > *para*. This type of decrease in dipole moment values has been observed by Murty¹⁴ for dihalobenzenes. This difference in the behaviour of the two series of compounds may be explained by considering the relative angles which the amino ($-\text{NH}_2$), methoxy ($-\text{OCH}_3$) and methyl ($-\text{CH}_3$) groups make with the conventional bond direction.

In toluidines the methyl group moment lies in the plane of benzene ring with its negative end towards the ring whereas the methoxy group in anisidines does not lie in the plane of benzene ring and makes certain angle with the conventional bond.³ The amino group is out of the plane of the benzene ring for both the (anisidine and toluidine) cases. Out of the plane group moment (amino and methoxy) can change their relative direction with each other. Therefore, this requires averaging over all possible position around the bond for the calculation of the dipole moment.

For molecule containing freely rotating group, Eyring¹⁵ gave a general equation for the resultant moment. For disubstituted benzene, the equation reduces to

$$\mu^2 = \mu_{01}^2 + \mu_{02}^2 + C \mu_{01} \mu_{02} \cos \theta_1 \cos \theta_2 \quad (2)$$

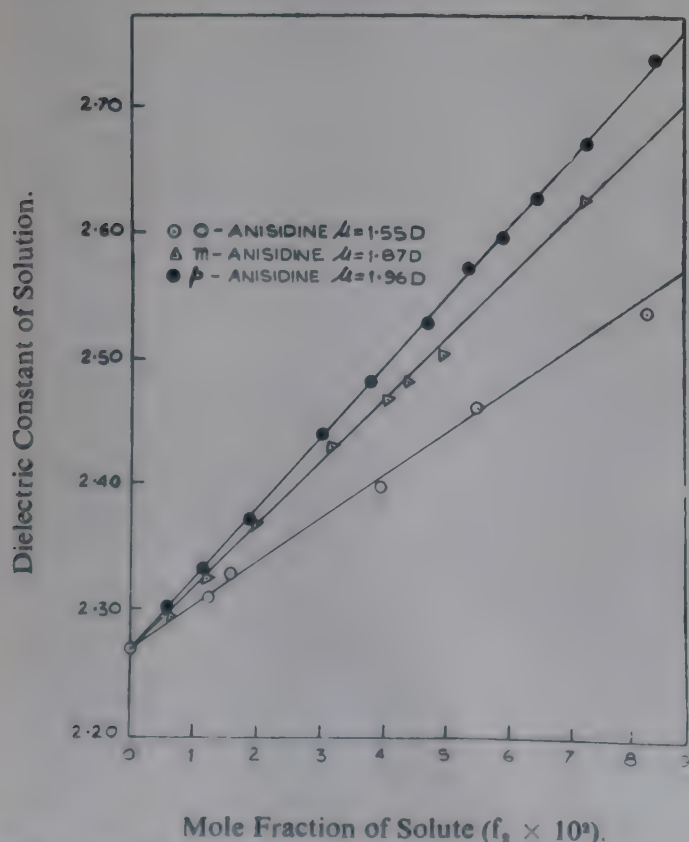


Fig. 1—Variation of Dielectric Constant of Solution against Mole fraction of Solute.

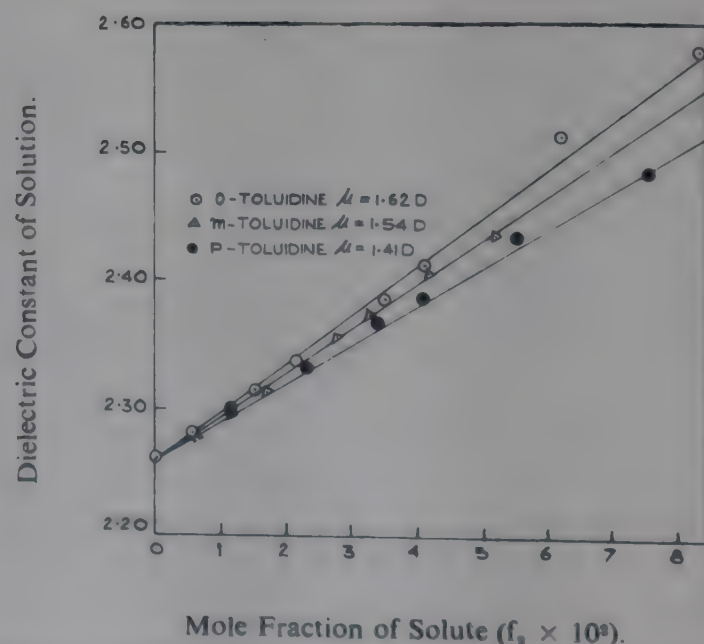


Fig. 2—Variation of Dielectric Constant of Solution against Mole Fraction of Solute.

where μ_{01} and μ_{02} are the group moments, θ_1 and θ_2 are their inclinations to the valence bond and $C=1, -1$, and -2 for *ortho*, *meta* and *para* substitution respectively. The group moment values and their angles with the conventional bond are given in Table 2. The values calculated with the help of equation (2) are included in Table 1. They are not in good agreement with the observed values. But the order of increase and decrease in the dipole moment values follows a pattern similar to the experimental values. The agreement between the experimental and theoretically calculated values improves if the

TABLE 2*—VALUES OF GROUP MOMENT, THE ANGLE SUBTENDED BY THE CONVENTIONAL BOND AND THE POLARIZABILITY OF THE SUBSTITUENTS USED FOR CALCULATING THE DIPOLE MOMENT

Substituent	Group Moment Debye	Angle Degree	Polarizability $\times 10^{24}$
$-\text{CH}_3$	0.37	180	2.45
$-\text{OCH}_3$	1.25	55	2.06
$-\text{NH}_2$	1.53	142**, 134***	1.97

* Smyth, C. P., *Dielectric Behaviour and Structure* (McGraw Hill Book Co. Inc. New York), 1955, 253.

** The value calculated on the basis of *para* methyl compound as reference.

*** The value calculated on the basis of *para* chloro compound as reference.

induced effects are also taken into consideration as done by Smallwood and Herzfeld.¹⁶ Following this method¹⁶, the dipole moment values of all the six molecules have been calculated considering all the primary group moments, the corresponding angles and the polarizability values as given in Table 2. The calculated values (Table 1) are in better agreement with the experimentally observed values. A slight disagreement still exists which can quantitatively be explained on the basis of contribution arising from resonance of highly polar structures, *ortho* effect and steric hindrance, dealt in detail by Smith.³

The values of the dipole moment in gas phase (μ_G) may also be extrapolated from that observed in solution (μ_{sol}) by equation of Guggenheim.¹⁷

$$\mu_G = \frac{\epsilon_0 + 2}{3 \sqrt{\epsilon_0}} \mu_{\text{sol}} \quad (3)$$

where ϵ_0 is the value of dielectric constant of the solvent.

Higasi¹⁸ has given another equation for similar calculation.

$$\mu_G = \frac{\mu_{\text{sol}}}{1 + [(\epsilon_0 - 1)/(\epsilon_0 + 2)]} \quad (4)$$

where A is a constant depending on the diameter of the molecule. The value of A given by Desai and Pandhare¹⁹ has been used in the present calculation. The gas phase dipole moment values, thus calculated, are also included in Table 1. The gas phase experimental value of dipole moment of *o*-anisidines (1.62 D) given by Link²⁰ is in good agreement with the present extrapolated value, calculated on the basis of Higasi equation.

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The author is grateful to Prof. S. Chandra under whose supervision the present work was done. Thanks are due to Drs. J. Prakash and R. A. Yadav, Physics Department, University of Gorakhpur, for their active cooperation. He is also thankful to Sri K. C. Banerji and Dr. B. S. Sastry of the Planning and Development Division, FCI Ltd. Sindri, for their help and encouragement.

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This paper deals with the results of pilot plant investigation for the evaluation of three different experimental batches of catalyst developed by this Division of FCI Ltd. The pilot plant was a commercial scale one using two of reformer tubes $3\frac{1}{8}$ i.d. $\times$ $4\frac{1}{2}$ o.d. $\times$ 17' long (heated length 13.5 ft.).

Performance studies were made for periods extending upto 340-500 hrs. The data were analysed on the basis of simplified reaction mechanism proposed by Ghosal *et al.* The performance characteristics of the three catalysts tested were as follows: The activity of the catalyst PR-C-2 was less than that of PR Misc. 40, but PR-C-2 was the most stable and least susceptible to varbon deposition and hence most suitable for industrial use.

Run No.	Catalyst Used	Temperature, °C	Pressure, psia	S/C. Ratio, moles atm.	Period of Run, hr	Maximum Pressure Drop, psi	Activity Factor
8.	PR Misc. 40 6% C ₂ O, 12% NiO	810-820	210-237	3.5-6.0	340	20.0	9.0×10^{-2}
10.	PR-203D 8% C ₂ O, 12% NiO	793-810	167-188	3.3-4.6	430	12.5	3.55×10^{-2}
11.	PR-C-2 8% C ₂ O, 12% NiO *(method of preparation was different from that of PR-203D)	800-825	185	3.0-4.20	500	6.5	6.7×10^{-2}

Development of Rate Equation for Steam Hydrocarbon Reforming*

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Introduction

Steam-reforming of low molecular weight hydrocarbons for synthesis gas production started in 1930s with catalytic reforming of natural gas at atmospheric pressure in multi-tubular reactors operating around 850°C. Subsequently, after the second World War, steamreforming of higher molecular weight feedstocks was perfected. This was possible since in early 1960, I.C.I. developed their selective catalyst, which enabled reforming of higher molecular weight hydrocarbons at much lower steam-to-carbon ratio without any carbon deposition. Kurt Von Peters, Max Rudolf, William A. Read¹ etc. have done some studies on kinetics of hydrocarbon-steam reaction.

* Paper read at the Silver Jubilee Session of the Indian Institute of Chemical Engineers held at New Delhi during Dec. 3-6, 1972.

P & D Division of FCI Ltd has also done some bench and pilot scale investigations on naphtha-steam reforming using FCI developed catalysts.

The present paper deals with the results of pilot plant investigations carried out with a view to evaluate the performance of 3 different experimental batches of catalyst developed in this laboratory in order to find their industrial suitability.

Theory and Mechanism of Reaction

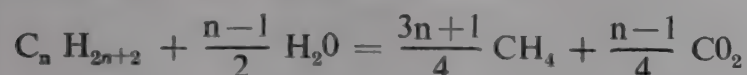
The reactions between hydrocarbon and steam are too complex. According to the mechanism postulated by Bridger *et al.*², naphtha is catalytically cracked in the initial stages of reaction into methane and unsaturated hydrocarbons as primary products, which subsequently react with steam producing carbon

monoxide, carbon dioxide, hydrogen and methane. In the hotter regions of the reformer, homogenous thermal reactions crack more of the feedstock to smaller saturated and unsaturated hydrocarbons which are then steam-reformed to carbon monoxide and dioxide, hydrogen and methane. The water gas-shift reaction is established rapidly and methane-steam reaction less rapidly. Ultimately at the exit end of the reactor, the reforming reactions are controlled by only methane-steam and shift reactions.

As early as 1964, one of the present authors³ assumed that higher paraffinic hydrocarbons undergo initial methanation reaction, which goes to completion at the feed end of the reactor (400-600°C), and the form of methanation reaction was given as:



Subsequently in 1965, Dent⁴ proposed a similar mechanism in the following form:



The mechanism proposed by these workers is too simple but, nevertheless, provides a practical and easy method for analysing kinetic data on steam-reforming.

The methanation reactions proposed by these workers are more or less identical but the equation proposed by Dent⁴ is thermodynamically more plausible⁵. However, bench scale data on steam-heptane reaction⁶ and pilot plant data on naphtha-steam reforming in a 24" i.d. reactor could be successfully correlated based on methanation reaction proposed by Ghosal *et al*⁷. Hence, for the analysis of the present series of pilot plant data, the same type of mechanism as proposed by Ghosal *et al*³, was adopted.

Experimental

Description of Pilot Plant: The pilot plant was an integrated one having a hydrodesulphurizer in the upstream of the reformer and cooler condenser, separator, high temperature and low temperature shift reactors in the downstream. All the catalytic reactors were charged with FCI developed catalysts viz., reforming catalyst in the reformer, ferric oxide-chromium oxide catalyst in high temperature shift reactor and copper oxide-zinc oxide catalyst in the low temperature shift reactor. Comox catalyst along with zinc oxide was charged in the hydrodesulphurizer. A process flow diagram of the whole plant, along with various controls, is shown in Fig. 1.

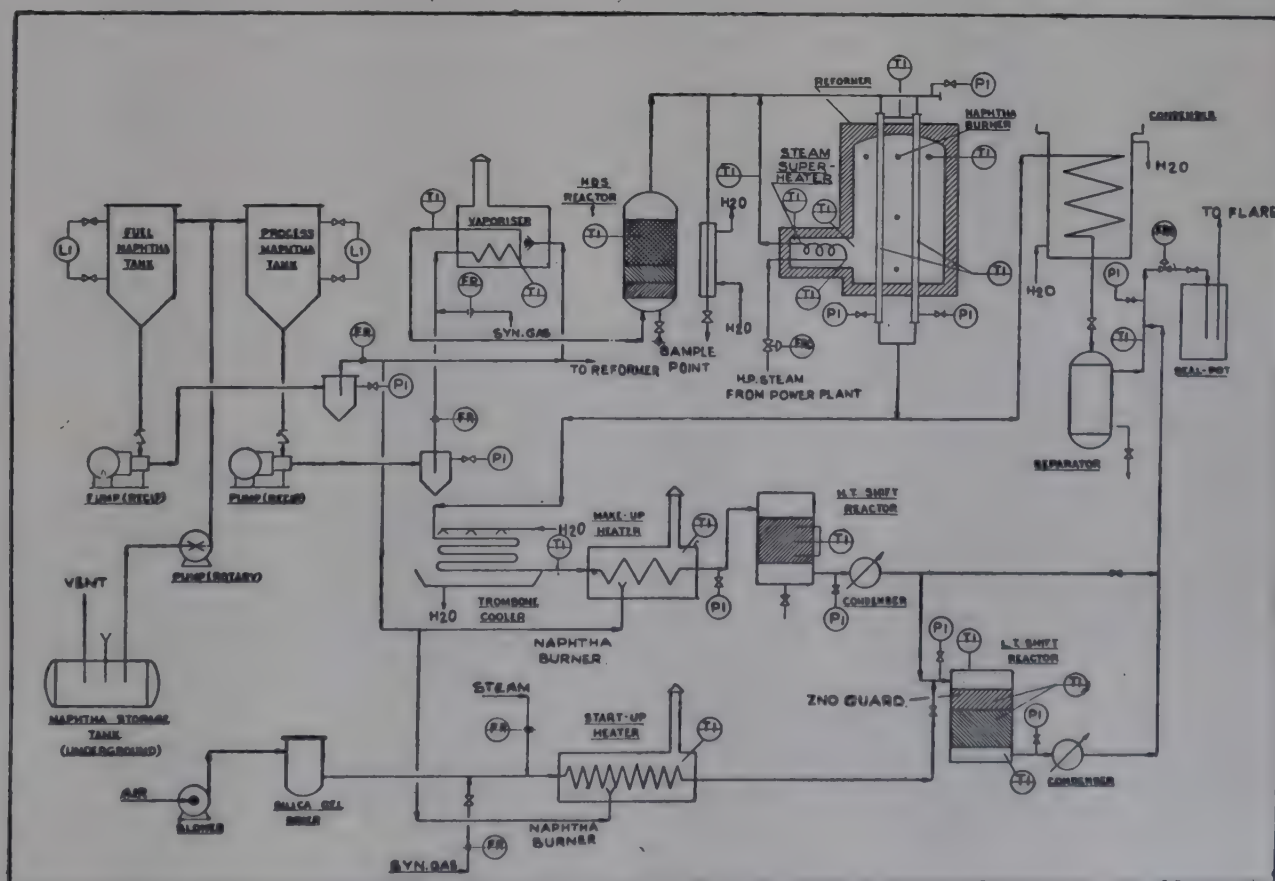


Fig. 1—Flow Diagram of Naphtha-Steam Reforming pilot Plant

The present paper deals with performance of a reforming catalyst charged in the reformer tubes and operated under commercial conditions. The reformer furnace was rectangular in cross-section and lined with firebricks. The heat required for the reforming reaction was supplied by fuel naphtha burners, placed horizontally at three different levels. To fulfil the high demand of heat at the top level, more numbers of burners were placed there. Two reformer tubes of H. K. alloy, 3-9/16" i.d. $\times$ 4 5/8" o.d. and 17 1/4' long were placed vertically inside the furnace having a heated length of 13' 6". The flanges at the bottom ends of the tubes were kept blanked during normal operation but this facilitated discharge of catalysts. Desulphurized vapour naphtha together with the proportionate quantity of steam entered into the tube through restricted orifices installed at the top to improve distribution of feed into the two tubes and the reformed gas goes out from the bottom to a common manifold via incoloy pigtails and from there to subsequent downstream equipments.

The flue gases were sucked out of the furnace via the flue gas steam superheater by the draft produced by a venturi draft arrangement. The position and layout of the reformer tubes, burners, flue duct, refractory lining, thermocouples, etc. are shown in Fig. 2.

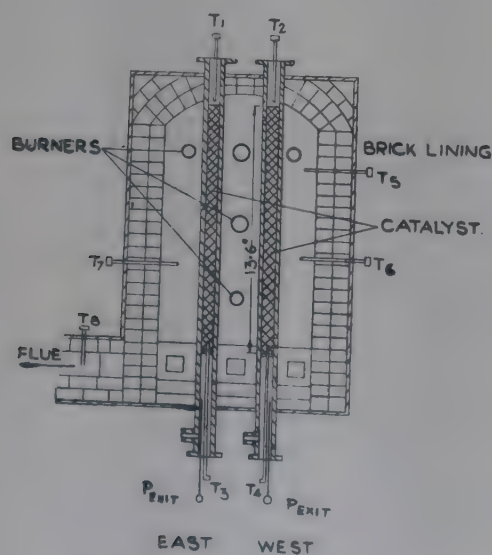


Fig. 2—Primary Raformer of the Steam-Naphtha Reforming Pilot Plant

The hydrodesulphurizer in the upstream of the reformer was charged with 10 kg. of FCI zinc oxide prills of 3-5 mm. size at the bottom. 80 kg. of Comox catalyst tablets of 5 mm. $\times$ 5 mm. size was charged above this and over this another layer of FCI-make 40 kg. Zinc Oxide catalyst prills of 3-5 mm. size were charged. A sketch of the hydrodesulphurizer along

with position of zinc oxide and Comox catalyst beds are shown in Fig. 3.

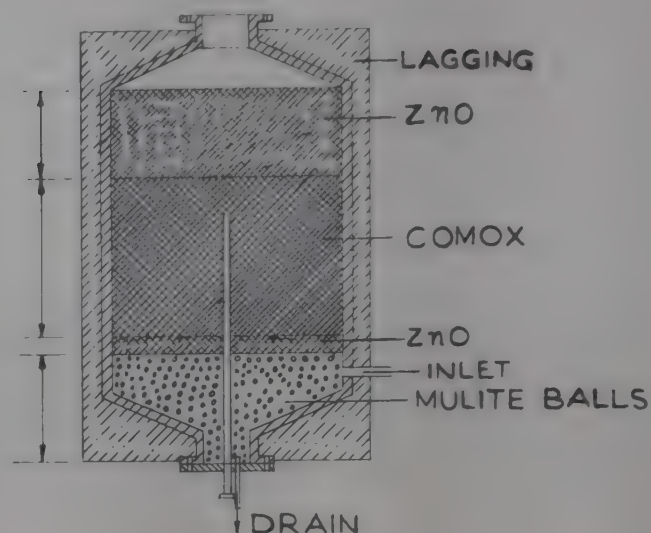


Fig. 3—Hydrodesulphurization Reactor of the Steam-Naphtha Reforming Pilot Plant

The reformer catalysts of FCI-make, whose performance were tested for an extended period of time in the pilot unit, were as follows :

Run No.	8	10	11
Type of Catalyst (all FCI-make)	PR Misc. 40	PR—203 D	PR—C—2
Composition	6% CaO, 12% NiO	8% CaO, 12% NiO	8% CaO, 12% NiO*
Shape	rings	rings	rings
Size	16mm. o. d. x. 6mm. i. d. x 16mm. long.	16mm. o. d. x. 6mm. o. d. x. 16mm. long.	16mm. i.d.x 6mm. o.d.x 16mm. long.
Weight of catalyst charged in			
Tube no. 1	32.0 Kg	25.08 Kg.	23.85 Kg.
Tube no. 2	32.0 Kg	24.90 Kg.	23.55 Kg.

* Method of preparation was different from that of PR—203D.

During the 8th and 11th runs naphtha from Barauni refinery was used as a feedstock and during 10th run naphtha from Cochin refinery was used.

Naphtha Specification: The specifications of the naphtha feedstock were as follows :

	8th Run	10th Run	11th Run
Source	Barauni	Cochin	Barauni
Boiling range, °C	40—140	—	—
Saturated hydrocarbon, % by wt.	84.4	95.5	83.3
Aromatics, % by wt.	15.0	4.0	16.5
Olefins, % wt.	0.6	0.43	0.2

The specifications of the reformer tubes were as follows :

Make	TEC, Japan
Material of construction	ASTM, 297, Centrifugally cast H.K. alloy
Tube, i.d.	3— $\frac{9}{16}$ "
Tube, o.d.	4— $\frac{3}{8}$ "
Tube length	17 $\frac{1}{2}$ '
Tube heated length	13 $\frac{1}{2}$ '
No. of tubes	2

Process Description: After the reformer tubes had been filled with catalyst and properly boxed up, fuel naphtha burners were lighted up one by one and blower started to supply air to the burners. Nitrogen from the Gas Reforming Plant was then allowed to flow through the reformer tubes and burners were lighted up. The firing rate was so adjusted that the temperature of the gas exit reformer rose at about 15-20°C/hr. When the exit gas temperature reached around 500°C, superheated steam was slowly introduced with the help of a flow recorder-controller into the reformer along with nitrogen. The steam flow rate was gradually increased to 200 kg./hr. When the temperature reached 700-750°C, catalyst reduction started. After reaching a stable condition at 700-750°C with steam flowing at about 200 kg./hr. synthesis gas, (hydrogen 69 per cent along with carbon monoxide and dioxide, etc.) available from the exit of water scrubber of ammonia plant, was fed at the inlet of hydrodesulphurizer. Gradually the nitrogen flow was cut off. When the temperature reached 800-820°C, the burners were controlled to maintain this temperature steady for the next 24 hours. During that period the gas exit reformer was frequently analysed to find when reduction was complete. When the analyses of gas at the inlet and exit became same a complete reduction was ensured. After reduction was over, naphtha was slowly introduced into the reformer, and the load brought upto approx. 25 kg./hr. keeping steam flow rate constant. The reformer inlet and outlet temperatures were maintained constant around 480°C and 800°C respectively. The tube skin temperature was never allowed to go beyond 920°C with the help of an optical pyrometer. The flue gas outlet temperature was maintained around 950°C.

After running for about 30-50 hours, naphtha throughout was increased slowly in a stepwise fashion and the steam flow decreased simultaneously so as to vary the steam/carbon ratio widely.

Results and Discussion

Earlier, some pilot plant studies on naphtha-steam reforming were done in a 2 $\frac{1}{4}$ " i.d. reformer tube⁷. In those experiments, FCI—developed rare earth-promoted catalyst was used and the operating conditions were limited to 7 ata pressure, 830-840°C exit reformer temperature and steam-to-carbon ratios from 4 to 8 moles of steam per carbon atom in feed. Specific object of the above test was to evaluate the suitability of FCI-developed catalyst for commercial application in synthesis gas preparation for methanol manufacture. The present series of pilot plant tests were done in bigger sized pilot plant with recently developed alkaline earth catalysts and the specific objective was to evaluate their activities and suitabilities for use in commercial reformers for both methanol and ammonia synthesis gas manufacture.

The results of the present series of pilot plant investigations using three different experimental batches of catalyst have been tabulated (Tables 1-3).

(a) **Catalyst Activity:** The experimental data for the different runs were analysed on the same basis as was done earlier by Ghosal *et al*⁷ and the data were correlated by plotting r/x against $\frac{C_{H_2}}{C_{H_2O}}$ in a log-log graph (Fig. 4). It was found that approximate straight line correlations are obtained for all the three

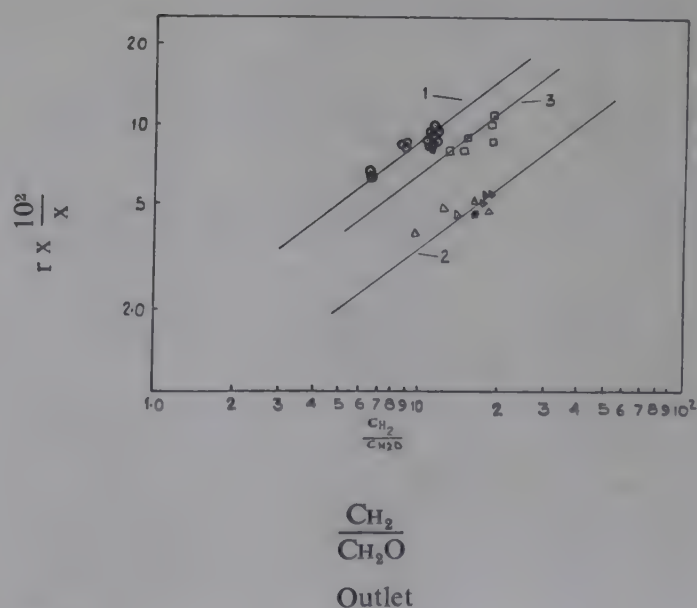


Fig. 4—

- 1—For TR MISC 40 Catalyst used During 8th Run
- 2—For PR 203D Catalyst used During 10th Run
- 3—For PR C-2 Catalyst used During 11th Run

different catalysts. From these correlations the rate equations for these catalysts may be put in the form :

$$r = A \left[\frac{C_{H_2}}{C_{H_2O}} \right]^m X$$

TABLE 1A--SAMPLE DATA OF REFORMER PERFORMANCE DURING VARIOUS RUNS
[S. V. 0.93 kg/hr (lt. of catalyst); Run No. 8 (using PR Misc-40 catalyst); Hours of run: 340]

Sl. No.	Inlet Pressure, psia	Average Pressure Drop, psi	Naphtha Flow Rate, kg./hr.	Stream Flow Rate, kg./hr.	Mass Velocity G, lb./hr. ft. ²	S/C Ratio, moles/atom	Outlet Temp., °C	Outlet Gas Composition, %dry					Equilibrium Methane at outlet		Equilibrium Temp., Approach, °C
								CO	CO ₂	CH ₄	H ₂	Rest	%dry	%wet	
1.	212.7	5.0	25.2	195.0	3390	6.0	820	8.8	16.2	1.1	73.9	Traces	0.420	0.197	780 40
2.	217.7	6.0	30.2	230	4100	5.9	820	8.8	16.6	1.2	73.4	"	0.470	0.220	780 40
3.	236.7	12.0	41.5	254	4543	4.77	810	9.6	16.0	1.6	72.8	"	1.25	0.680	798 12
4.	226.7	11.0	41.5	254	4543	4.77	810	9.6	16.4	1.6	72.4	"	1.18	0.634	794 16
5.	234.7	12.5	41.5	254	4543	4.77	810	9.6	16.0	1.6	72.8	"	1.22	0.664	796 14
6.	234.7	11.5	45.3	235	4309	4.00	810	12.0	14.0	2.2	71.8	"	1.98	1.188	806 4
7.	234.7	12.0	45.3	235	4309	4.00	810	12.6	13.2	2.2	72.0	"	1.97	1.190	805 5
8.	229.7	11.0	47.2	235	4185	3.72	810	13.0	13.2	2.4	71.4	"	2.23	1.368	807 3
9.	226.7	10.0	47.2	235	4185	3.72	810	14.2	12.8	2.4	70.6	"	2.21	1.335	806 4
10.	219.7	12.0	47.2	235	4185	3.72	810	13.0	13.6	2.4	71.0	"	2.10	1.287	803 7
11.	222.7	11.0	49.5	235	4220	3.54	810	13.8	14.0	2.8	69.4	"	2.45	1.475	805 5
12.	234.7	20.0	49.5	235	4220	3.54	810	13.2	13.6	2.8	70.4	"	2.49	1.552	806 4

TABLE 1B--SAMPLE DATA OF REFORMER PERFORMANCE DURING VARIOUS RUNS
[Run No. 8 (Using PR Misc-40 catalyst); Hours of run 340]

Sl. No.	Gas at Exit kg./moles/hr.					Total	(hr)/(ft ³) catalyst	Partial Press of CH ₄ (atm)a				Pressure psia		(PCH ₄) ⁻⁻⁻ (PCH ₄) log mean	0.59 G	Mean Mol. Wt. Mm	0.10 μ	X	10 ² r _x	CH ₃ CH ₃ O		
	CO	CO ₂	CH ₄	H ₂	Rest			H ₂ O	“r” lb. Moles CO+CO ₂		PCH ₄		(PCH ₄) eq Outlet								Inlet	Outlet
									(hr)/(ft ³)	CO+CO ₂	PCH ₄ Inlet	PCH ₄ Outlet										
1.	0.609	1.120	0.076	5.110	—	7.873	14.788	1.992	1.54	0.0726	0.0278	212.7	207.7	15.91	120.78	14.86	0.791	30.45	6.54	0.65		
2.	0.716	1.350	0.098	5.97	—	9.283	17.417	2.383	1.60	0.0833	0.0326	217.7	211.7	16.10	134.28	14.92	0.791	35.80	6.66	0.644		
3.	1.043	1.739	0.174	7.90	—	9.092	19.948	3.210	2.10	0.1332	0.1041	236.7	224.7	17.90	143.85	14.57	0.791	36.70	8.75	0.877		
4.	1.029	1.758	0.1715	7.75	—	9.247	19.956	3.220	2.01	0.1261	0.0930	226.7	215.7	17.20	143.85	14.58	0.791	35.00	8.47	0.838		
5.	1.043	1.740	0.174	7.91	—	9.082	19.949	3.210	2.08	0.1320	0.1002	234.7	222.2	17.78	143.85	14.38	0.791	38.00	8.45	0.878		
6.	1.389	1.620	0.255	8.31	—	7.731	19.305	3.470	2.417	0.2002	0.1802	234.7	223.2	18.10	139.39	14.03	0.791	37.00	9.39	1.074		
7.	1.468	1.538	0.256	8.39	—	7.648	19.300	3.470	2.417	0.2013	0.1806	234.7	222.7	18.10	139.39	13.87	0.791	37.40	9.29	1.098		
8.	1.531	1.556	0.283	8.41	—	7.419	19.199	3.560	2.516	0.2197	0.2040	229.7	218.7	17.72	136.67	13.89	0.791	36.70	9.70	1.132		
9.	1.622	1.462	0.275	8.07	—	7.496	18.925	3.560	2.483	0.2140	0.1970	226.7	216.7	17.64	136.67	14.41	0.791	35.60	10.00	1.077		
10.	1.508	1.578	0.378	8.23	—	7.329	18.923	3.560	2.408	0.2075	0.1815	219.7	207.7	17.00	136.67	13.98	0.791	40.60	8.78	1.122		
11.	1.590	1.613	0.323	8.00	—	7.619	19.145	3.700	2.543	0.2425	0.2123	222.7	211.7	17.48	137.73	14.30	0.791	42.00	8.81	1.050		
12.	1.574	1.622	0.334	8.40	—	7.197	19.127	3.690	2.680	0.2550	0.2270	234.7	214.7	18.20	137.73	13.98	0.791	42.00	8.79	1.167		

TABLE 2A—SAMPLE DATA OF REFORMER PERFORMANCE DURING VARIOUS RUNS

[S. V. 0.85 kg/hr (lit. of catalyst); Run No. 10 (using PR—203D catalyst); Hours of run: 430]

Sl. No.	Inlet Pressure, psia	Average Pressure Drop, psi ^a	Naphtha Flow Rate, kg./hr.	Steam Flow Rate, kg./hr.	Mass Velocity "G", lb./hr. ft.	S/C Ratio, moles/atom	Outlet Temp., °C	Outlet Gas Composition, %dry					Equilibrium Methane at outlet		Equilibrium Temp Approach °C
													%dry	%wet	
								CO	CO ₂	CH ₄	H ₂	Rest			
1.	167.7	2.5	25.0	150	2785	4.60	810	7.5	11.4	2.10	79.0	0.96	0.546	765	45
2.	172.7	2.5	28.8	150	2847	4.00	803	13.2	12.0	2.8	72.0	1.58	0.178	780	23
3.	170.7	3.0	31.0	150	2883	3.77	803	14.2	10.6	2.4	72.8	1.76	1.120	784	19
4.	174.7	2.5	34.0	150	2930	3.44	803	12.2	11.2	3.0	73.6	2.22	1.56	786	17
5.	172.7	3.0	30.6	145	2780	3.60	793	12.80	10.2	3.00	74.0	2.34	1.618	775	18
6.	172.7	2.5	30.6	145	2780	3.60	795	12.17	10.23	2.80	74.80	2.31	1.644	780	15
7.	170.7	2.5	30.6	145	2780	3.60	793	12.38	10.52	3.20	73.90	2.34	1.612	773	20
8.	170.7	2.5	30.6	145	2780	3.60	795	12.80	10.20	3.00	74.00	2.27	1.540	778	17
9.	177.7	3.0	34.5	150	2940	3.37	810	13.5	9.85	3.00	73.65	2.08	1.485	793	17
10.	182.7	5.5	35.3	150	2955	3.31	815	13.30	10.65	2.80	73.25	2.11	1.497	798	17
11.	184.7	7.5	35.3	150	2955	3.31	805	13.53	10.53	3.25	72.69	2.38	1.658	780	15
12.	188.7	12.5	34.0	150	2930	3.44	810	12.60	11.20	2.80	73.4	1.98	1.373	795	15

TABLE 2B—SAMPLE DATA OF REFORMER PERFORMANCE DURING VARIOUS RUNS

[Run No. 10 (using PR —203D catalyst); Hours of run 430]

Sl. No.	Gas at Exit, kg./moles/hr.				Total	H ₂ O	Rest	CO	CO ₂	CH ₄	H ₂	“r” lb. Moles CO + CO ₂ (hr)/(ft ³) catalyst	Partial Press of CH ₄ (atm)a			Pressure psia		(PCH ₄ - PCH ₄) eq log mean	(P + 2p CH ₄) log mean	G	Mean Mol. Wt. Mm	0.10 μ	X	10 ² rx	CH ₃ CH ₂ O	
	CO	CO ₂	CH ₄	H ₂									PCH ₄ Inlet	PCH ₄ Outlet	(PCH ₄) eq	(PCH ₄) Outlet	Inlet									Outlet
1.	0.501	0.761	0.138	5.278	12.154	1.561	1.53	0.1277	0.0616	167.7	165.2	0.452	12.90	108.45	13.93	0.792	39.0	4.008	0.964							
2.	1.041	0.947	0.221	5.68	12.78	2.342	1.87	0.2003	0.1267	172.7	170.2	0.527	13.62	110.15	13.60	0.792	44.7	5.04	1.260							
3.	1.152	0.861	0.195	5.91	12.831	2.376	1.85	0.1732	0.1270	170.7	167.7	0.462	13.17	110.15	13.24	0.792	41.7	5.69	1.254							
4.	1.120	1.029	0.275	6.755	13.087	2.537	2.04	0.2464	0.1823	174.7	172.2	0.531	13.96	111.17	12.61	0.792	47.85	5.30	1.728							
5.	1.093	0.871	0.256	6.32	12.363	2.320	1.945	0.2400	0.1866	172.7	169.7	0.487	13.74	108.39	12.50	0.792	43.90	5.29	1.653							
6.	1.072	0.902	0.247	6.59	12.382	2.328	1.945	0.2312	0.1907	172.7	170.7	0.454	13.71	108.39	12.22	0.792	41.90	5.56	1.846							
7.	1.052	0.895	0.273	6.29	12.330	2.297	1.922	0.2535	0.1847	170.7	168.2	0.515	13.51	108.39	12.52	0.792	47.10	4.875	1.647							
8.	1.093	0.871	0.256	6.32	12.363	2.320	1.922	0.2375	0.1762	170.7	168.2	0.502	13.61	108.39	12.50	0.792	45.70	5.07	1.653							
9.	1.268	0.935	0.282	6.915	13.159	2.582	2.112	0.2547	0.1762	177.7	174.7	0.577	14.20	111.70	12.36	0.792	52.70	4.90	1.836							
10.	1.248	0.971	0.300	6.703	13.218	2.619	2.155	0.2382	0.1730	182.8	177.2	0.571	14.42	111.80	12.69	0.792	49.85	5.26	1.678							
11.	1.252	0.938	0.329	6.61	13.159	2.58	2.178	0.2988	0.2086	184.7	177.2	0.610	14.59	111.80	12.72	0.792	52.43	4.915	1.642							
12.	1.149	1.021	0.255	6.69	13.128	2.56	2.203	0.2333	0.1648	188.7	176.2	0.578	14.68	111.17	12.70	0.792	49.50	5.18	1.665							

TABLE 3A—SAMPLE DATA OF REFORMER PERFORMANCE DURING VARIOUS RUNS
[S. V. 0.9 kg/hr lit. of cat.); Run No. 11 (Using PRC-2 catalyst); Hours of run 500]

Sl. No.	Inlet Press, psia	Aver- age Press Drop psia	Naph- tha Flow rate kg/hr	Steam Flow Rate, kg/hr	Mass Velocity, G lb/(hr) (ft ²)	S/C Ratio, Moles/atom	Out- let Temp °C	Outlet Gas Composition, % dry					Equilibrium Methan at Outlet		T _{0.14} °K		
								CO	CO ₂	CH ₄	H ₂	Rest	% Dry	% Wet		Temp °C	Ap- proach °C
1.	185.4	6.5	23.60	128	2415	4.20	820	10.0	15.20	1.40	72.2	1.2	1.10	0.660	805	15	2.662
2.	185.4	6.5	26.745	130	2495	3.77	825	14.0	12.60	1.70	70.4	1.3	1.35	0.825	812	13	2.663
3.	185.4	5.5	28.320	131	2540	3.60	820	13.80	12.00	2.00	70.7	1.5	1.65	1.063	810	10	2.662
4.	185.4	5.5	30.285	134	2620	3.44	820	14.20	11.20	2.10	71.1	1.4	1.78	1.192	813	7	2.662
5.	185.4	5.5	31.465	134	2635	3.31	810	14.30	11.10	2.60	70.6	1.4	2.40	1.632	805	5	2.661
6.	185.4	5.5	33.274	131	2615	3.05	805	13.20	11.40	3.30	70.8	1.3	3.10	2.240	800	5	2.660
7.	185.4	5.5	33.274	131	2615	3.05	800	13.20	11.30	3.40	70.8	1.3	3.35	2.430	797	3	2.660
8.	185.4	5.5	35.477	131	2745	3.00	800	13.80	11.00	3.60	70.3	1.3	3.50	2.530	795	5	2.660

TABLE 3B—SAMPLE DATA OF REFORMER PERFORMANCE DURING VARIOUS RUNS
[Run No. 11 (Using PR C-2 catalyst); Hours of run 340]; S.V.=0.90 kg./lit. of catalyst]

Sl. No.	Gas at Exit, kg./moles/hr.				"r" In. Moles CO+CO ₂ (hr) (ft ³ catalyst)		Partial Press of CH ₄ (atm)a		Pressure psia		(PCH ₄ -PCH ₄ eq) log mean	(P+2p CH ₄) log mean	G ^{0.50}	Mean Mol. Wt. Mm	μ ^{0.10}	X	10 ³ $\frac{\text{CH}_2}{\text{CH}_2\text{O}}$				
	CO	CO ₂	CH ₄	H ₂	Rest	H ₂ O	Total	PCH ₄ Inlet	PCH ₄ Outlet	(PCH ₄) eq								Inlet	Outlet		
1.	0.645	0.980	0.091	4.685	0.079	4.271	10.721	2.580	2.080	0.1032	0.0850	185.4	178.9	0.420	14.32	99.3	14.10	0.79	29.6	8.71	1.090
2.	0.961	0.866	0.117	4.840	0.096	4.381	11.261	2.900	2.290	0.1264	0.1000	185.4	178.9	0.490	14.65	99.6	14.09	0.79	33.9	8.55	1.105
3.	1.020	0.886	0.148	5.230	0.106	4.887	11.477	3.025	2.380	0.1580	0.1300	185.4	179.9	0.506	14.69	101.8	13.69	0.79	36.7	8.25	1.280
4.	1.133	0.895	0.168	5.685	0.099	3.902	11.982	3.220	2.470	0.1731	0.1460	185.4	179.9	0.515	14.85	104.2	13.33	0.79	38.8	8.30	1.455
5.	1.164	0.904	0.212	5.750	0.110	3.835	11.975	3.285	2.555	0.2164	0.2000	185.4	179.9	0.471	14.93	104.5	13.31	0.79	35.4	9.29	1.500
6.	1.140	0.984	0.285	6.110	0.115	3.287	11.921	3.380	2.730	0.2920	0.2740	185.4	179.9	0.495	15.05	104.1	12.96	0.79	37.9	8.91	1.859
7.	1.140	0.975	0.294	6.110	0.115	3.270	11.904	3.360	2.730	0.3020	0.2970	185.4	179.9	0.392	15.21	104.1	12.91	0.79	29.8	11.28	1.870
8.	1.248	0.994	0.325	6.355	0.118	3.449	12.489	3.562	2.772	0.3180	0.3093	185.4	179.9	0.434	15.30	107.1	12.98	0.79	33.6	10.50	1.843

where m is approximately 0.6 for all the catalysts and 'A' the activity factor depends on the type of catalyst. The values of 'A' for the different catalysts have been shown in Table 4.

(b) *Performance Characteristics*: Though PR Misc 40 was the most active catalyst, it was the least stable of the three as was evident from the pressure drop characteristics (Table 4). All the three catalysts after discharging from the reactor were found intact and free of any carbon deposition. The observed increase in pressure drop, in case of PR misc 40 was explained on the basis that there was slight carbon deposition during reforming reaction which during planned shut-down was reacted away by steam at elevated temperature. Of the three catalysts tested, PR-C-2 had the highest stability as was evident by constant pressure drop characteristics and there was no carbon deposition as well. PR-C-2 had also quite a high activity though slightly less than PR Misc 40. From the results of these studies, it can be concluded that PR-C-2 will have a high suitability as an industrial catalyst. It has, therefore, been planned that this catalyst will be subsequently subjected to more stringent operating conditions in the pilot testing unit.

(c) *Equilibrium Approach*: The equilibrium approach for methane steam reaction for the three different catalysts has been shown in Fig. 5. Equilibrium approach under different operating conditions is an easy method to judge the catalyst activity⁸. From Fig. 5 it is clear that equilibrium approach for all the three catalysts depends similarly with steam/carbon ratio. Higher the steam/carbon ratio, more is the equilibrium approach. Equilibrium approach is also high with lesser active catalyst as it should be and this has been clearly shown.

Along with these, the results of earlier pilot plant investigations² with CD-RN-19B catalyst in 2¼" i.d. reformer tubes at around 830-840°C, 97-107 psia—

pressure and S/C ratio ranging from 4.0 to 8.0 can be compared. It is seen that CD-RN-19B has more or less the same activity (activity factor = 6.85×10^{-2})

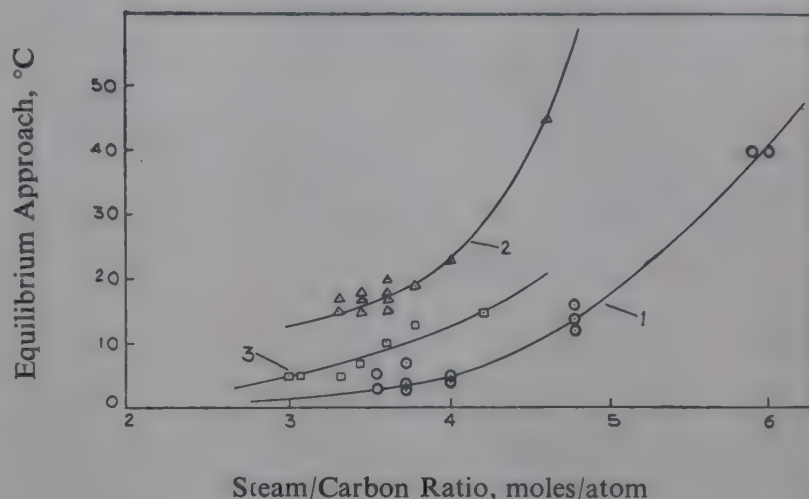


Fig. 5—
Legend
1. TR MISC Catalyst used During 8th Run
2. PR 203D Catalyst used During 10th Run
3. PRC-2 Catalyst used During 11th Run

as PR-C-2 but less stability compared to PR-C-2 as it is prone to carbon deposition (shown by high pressure drop) even at a S/C ratio as high as 4.0.

Nomenclature

$$G = \frac{G^{0.59} T^{0.14} (P_{CH_4} - P_{CH_4 eq}) \log \text{mean}}{\mu^{0.10} dp^{1.41} M_n (P + 2p_{CH_4}) \log \text{mean}}$$

dp = surface equivalent spherical diameter, ft.

G = Mass velocity across reformer tube, lb./(hr.)/(ft²).

M_m = Mean mol. wt. of steam gas mixture at outlet.

P = Total pressure at any point, atma

P_{CH_4} = Partial pressure of methane at any point, atma

$P_{CH_4 eq}$ = Eqbri. partial press. of methane at outlet, atma

TABLE 4

Run No.	Type of Catalyst	Temp. °C	Pressure psia	S/C ratio moles/atom	Period of run hrs.	Maximum pressure drop psi	Activity factor.
8.	PR Misc 40, 6% CaO, 12% NiO	810—820	210—237	3.5—6.0	340	20.0	9.0×10^{-2}
10.	PR—203D, 8% CaO, 12% NiO	793—820	167—188	3.3—4.6	430	12.5	3.55×10^{-2}
11.	PR+—C—2, 8% CaO, 12% NiO	800—825	185	3.0—4.20	500	6.5	6.7×10^{-2}

+ Its method of preparation was different from that of PR-203D

r = rate of reaction expressed
 $\frac{\text{lb moles (CO + CO}_2\text{)}}{(\text{hr.}) (\text{ft}^3 \text{ of catalyst})}$

T = outlet temperature of reformed gas, °K

μ = Viscosity of outlet steam gas mixture,
 $\frac{\text{lbs}}{(\text{hr.}) (\text{ft.})}$

$\frac{C_{\text{H}_2}}{C_{\text{H}_2\text{O}}} =$ Molar ratio of H_2 and steam at the exit
of reformer

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for their active interest shown during the preparation of this text.

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Experiments were conducted for two consecutive years on tomato using two levels of nitrogen and four methods of application to find out the efficacy of partial spray application of urea *vis-a-vis* respect to full soil application. Increase in the rate of nitrogen influenced the yield. Split application of nitrogen gave higher yield than single application in both the years, but the different methods of split did not show any significant difference in yield. At 120 kg. nitrogen level, four different methods of nitrogen application did not produce any significant difference in yield.

Nitrogen content of leaves increased with the increase in the levels of nitrogen in both the years. Foliar application gave higher nitrogen content at 60 kg. nitrogen level when compared with full basal application. Nitrogen content of leaves under various treatments had almost similar trend with yield character.

Relative Efficiency of Soil and Foliar Application of Urea on Tomato (*Lycopersicon esculentum* Mill.)

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Foliar application of urea has been used satisfactorily in a number of vegetables³⁻⁵. In the previous report on brinjal¹ the authors observed that at 40 kg. nitrogen level with half soil and half foliar, yield of brinjal was comparable to the yields obtained with 80 and 120 kg. soil application. The present experiment was designed to find out the efficacy of partial spray application of urea with respect to full soil application on tomato.

Material and Methods

The trial was conducted during the *Rabi* seasons of 1969-70 and 1970-71 using Sioux variety of tomato under irrigated condition in the experimental farm at Sindri. A factorial design with two levels of nitrogen (60, 120 kg./ha) and four methods of application with control was adopted. The different methods of fertilizer application were as under: (1) M_1 —Full basal; (2) M_2 —30 kg. nitrogen in two split doses as top dressing to soil and the rest as basal; (3) M_3 —15 kg. nitrogen as top dressing to soil and 15 kg. nitrogen as foliar; and (4) M_4 —30 kg. nitrogen as foliar in two splits and the rest as basal.

There were 9 treatment combinations including the control and they were replicated 4 times. Altogether, there were 36 plots with each net plot size of 14.4 sq. m. Seeds were sown in the later part of August and transplanting was done after one month

of sowing with the spacing of 60 cm. from plant to plant and 60 cm. from row to row. At the time of land preparation P_2O_5 and K_2O were applied at the rate of 60 kg./ha. The experiment was laid out in a field having the average pH 8.0, E.C. (m.mhos/cm.) 0.12; organic carbon (%) 0.221; available P_2O_5 (kg./ha) 30.51; available K_2O (Kg./ha.) 325.

Results and Discussion

Yield: Yield data were statistically analysed and are presented in Tables 1 and 2. Significant differences were observed between the methods and levels of fertilizer application. Yield of tomato averaged over four methods of fertilizer application was significantly higher at higher level of nitrogen application in both the years. At 60 kg.N/ha., the yield under each of M_2 , M_3 and M_4 methods of application was significantly higher than that of M_1 , but there was no significant difference in yield between M_2 , M_3 and M_4 . But at 120 kg.N/ha. level there was no significant difference in yield between the four methods of fertilizer application in both the years.

Although a significant difference in yield was found between 60 and 120 kg. N/ha. levels they were comparable under M_2 , M_3 and M_4 but significantly different under M_1 during 1969-70. Similar trend was noticed during 1970-71 excepting that under M_2 also significant difference in yield was present between

the two levels (i.e. 60 and 120 kg. N/ha.) of fertilizer application.

TABLE 1—EFFECT OF SOIL AND FOLIAR APPLICATION OF UREA AT VARYING LEVELS ON THE YIELD (TONNES/HA.) OF TOMATO DURING 1969-70

Methods	Full Basal (M ₁)	Basal N+15 kg. of N as top dressing to soil twice (M ₂)	Basal N+15 kg. of N as top dressing to soil and 15 kg. of N as foliar (M ₃)	Basal N+15 kg. of N as foliar twice (M ₄)	Mean
Level kg./ha.					
0			21.9		21.9
60	43.5	54.8	61.7	55.1	53.8
120	60.9	64.0	61.8	59.0	61.4

C.D. at 5% level between treatment means = 10.8 te/ha.

C.D. at 5% between level means excluding control = 5.4 te/ha.

TABLE 2—EFFECT OF SOIL AND FOLIAR APPLICATION OF UREA NITROGEN AT VARYING LEVELS ON THE YIELD (TONNES/HA.) OF TOMATO DURING 1970-71

Methods	Full Basal (M ₁)	Basal N+15 kg. of N as top dressing to soil twice (M ₂)	Basal N+15 kg. of N as top dressing to soil and 15 kg. of N as foliar (M ₃)	Basal N+15 kg. of N as foliar twice (M ₄)	Mean
Level kg./ha.					
0			26.6		26.6
60	45.7	55.6	63.4	60.6	56.3
120	62.9	68.5	69.5	63.9	66.3

C.D. at 5% level between treatment means = 11.1 te/ha.

C.D. at 5% level between level means excluding control = 5.6 te/ha.

Nitrogen Content of Leaves: Leaf samples from each treatment were collected 15 days after application of urea for analysis of nitrogen. Nitrogen content was influenced by increasing rate of urea application (Tables 2 and 3).

Just like yield at 60 kg. level, nitrogen content of leaves at each of M₂, M₃ and M₄ was significantly more than that of at M₁ i.e. full basal application, while between M₂, M₃ and M₄ and at 120 kg. N/ha. level no significant difference in nitrogen content was found. When fertilizer was applied by M₃ and M₄ methods, no significant difference in nitrogen content in leaves was noted between 60 and 120 kg. N/ha. levels in both the years, while by M₂ method, the difference was most significant during 1969-70 but non-significant during 1970-71 between 60 and 120 kg. level of nitrogen application.

TABLE 3—CONTENT OF NITROGEN EXPRESSED IN PERCENTAGES IN TOMATO LEAVES DURING 1969-70 UNDER DIFFERENT METHODS OF APPLICATION OF UREA AT VARYING LEVELS

Methods	Full Basal (M ₁)	Basal N+15 kg. of N as top dressing to soil twice (M ₂)	Basal N+15 kg. of N as top dressing to soil and 15 kg. of N as foliar (M ₃)	Basal N+15 kg. of N as foliar twice (M ₄)	Mean
Level kg./ha.					
0			2.38		2.38
60	2.79	2.89	3.48	3.29	3.10
120	3.30	3.35	3.50	3.45	3.41

C.D. at 5% level of the treatment means = 0.46

C.D. at 5% level between level means excluding control = 0.23

TABLE 4—CONTENT OF NITROGEN EXPRESSED IN PERCENTAGES IN TOMATO LEAVES DURING 1970-71 UNDER DIFFERENT METHODS OF APPLICATION OF UREA AT VARYING LEVELS

Methods	Full Basal (M ₁)	Basal N+15 kg. of N as top dressing to soil twice (M ₂)	Basal N+15 kg. of N as top dressing to soil and 15 kg. of N as foliar (M ₃)	Basal N+15 kg. of N as foliar twice (M ₄)	Mean
Level kg./ha.					
0			2.38		3.32
60	2.96	3.36	3.57	3.40	2.38
120	3.56	3.74	3.97	3.75	3.76

C.D. at 5% level of the treatment means = 0.44

C.D. at 5% level between levels means excluding control = 0.22

The results of the present study indicate that split application of nitrogen in tomato is superior to single basal application at 60 kg. level. But between the methods of split applications of nitrogen, i.e. in two top dressing, one foliar and one top dressing and two foliar sprays did not produce any significant difference in yield. At higher level (120 kg. N/ha.) of nitrogen application all the methods were at par. The highest level of nitrogen used in the experiment (120 kg./ha.) seemed to be slightly more than the optimal level of nitrogen requirement for Sioux variety of tomato under Sindri condition which was found to be 110 kg./ha. by the authors in some previous experiments². That is why when fertilizer was applied in slight excess to its requirement all the methods were appeared at par, but at lower level the efficiency of different methods were exhibited. The leaf analysis for nitrogen content under various treatments had also showed similar trend. The beneficial effect of foliar feeding in increasing yield has been reported by

a number of workers in vegetables³⁻⁵. But in the present experiment, application of urea in three splits was found to be as good as that of spray application. This is obvious because the judicious split application of nitrogen accounts for the lesser loss and better uptake of fertilizer nutrients by tomato plants. Hence, it may be concluded that the beneficial effect of foliar application of urea for better uptake and utilisation of nitrogenous fertilizers can also be obtained by its judicious split soil application in tomato.

Acknowledgement

The authors are thankful to Mr. K. P. Dasgupta, Statistician, Fertilizer Promotion & Agricultural

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K-dithiotrihydroxymethyl aminomethane has been used successfully as an analytical reagent for the amperometric titration of cadmium using ammonium tartrate-potassium nitrate (pH 8.0) as a supporting mercury electrode. Cadmium has also been determined in binary solutions with copper. The method is simple, precise and easy to adopt. Its accuracy is comparable with that of the conventional methods.

Amperometric Titration of Cadmium with K-Dithiotrihydroxymethyl Aminomethane and its Determination in the Presence of Copper

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Adam¹ developed a controlled current potentiometric method for the determination of cadmium with EDTA. Immig and Jander² estimated very dilute solution of cadmium with hydrogen sulphide solution conductometrically. Kalvoda and Zyka³ performed amperometric titration of cadmium with potassium ferricyanide. Stock⁴ made use of 8-hydroxyquinoline in the amperometric estimation of cadmium. Nikell and Cooke⁵ titrated cadmium amperometrically with EDTA. Amperometric determination of cadmium as tellurite has been reported previously from this laboratory⁶. In the present study, K-dithiotrihydroxymethyl aminomethane—a new analytical reagent—has been used as a titrant for the amperometric determination of cadmium, which has also been estimated in the presence of copper.

Polarographic characteristics of K-dithiotrihydroxymethyl aminomethane showed an irreversible, well-defined, anodic wave in various supporting electrolytes of different pH values (4.5-9.5). In 0.1M ammonium tartrate-potassium nitrate (pH 8.0), the half-wave potential ($E_{1/2}$) for the anodic wave of the reagent was found to be $-0.56V$ vs. SCE. The constancy of $i_d \sqrt{t_{H_2}}$ values indicated that the waves are diffusion-controlled. The diffusion current was found to be proportional to the concentrations of the reagent.

This has been utilized for developing an amperometric titration procedure for determination of cadmium and mixtures of cadmium and copper. Two methods have been developed the first based on the measurement of the anodic current of excess titrant after the end-point, and the second utilizing the decrease in height of the reduction wave of the uncombined metal ion during the course of titration. A combination of these two methods is used for the determination of the constituents of binary solutions containing copper and cadmium.

EXPERIMENTAL

Reagents

(1) Metal solutions of copper and cadmium were obtained from E. Merck's samples and standardized by gravimetric methods⁷. All other reagents used were of AnalaR variety.

(2) *Preparation & Standardization of K-Dithiotrihydroxymethyl Aminomethane* $[(CH_2OH)_3C-NH-C-SK]$:

$$\begin{array}{c} \parallel \\ S \end{array}$$

200 ml. of saturated solution of trihydroxymethyl aminomethane was taken in a beaker and 5g. of potassium hydroxide was added. The beaker was cooled in ice and then 10 ml. of carbon disulphide was added. The solution was stirred thoroughly with a magnetic stirrer for 16 hr. followed by a little addi-

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tion of carbon disulphide time to time. A deep yellow liquid was found with liberation of considerable amount of heat. The excess carbon disulphide was then removed by thorough shaking with double distilled pure benzene and the liquid was separated using a separating funnel. It was then evaporated a little by heating on a water bath and cooled in ice. A highly hygroscopic crystalline solid was separated. The reagent was standardized with potassium ferricyanide in alkaline medium in presence of osmium tetroxide as catalyst by amperometric titration at a potential of +0.2V vs SCE using rotating platinum micro-electrode.

Apparatus

Titration were carried out in a Fisher Electropode. Readings were taken using dropping mercury electrode as polarizable electrode and saturated calomel electrode with Agar-KCl bridge as non-polarizable electrode. pH measurements were made with a line operated Beckman Zeromatic pH meter.

Procedure

Preliminary observations showed that cadmium and copper were precipitated with the reagent in ammonium tartrate-potassium nitrate base electrolyte. The appropriate operative conditions for the quantitative estimation were established by trial experiments. It was observed that copper and cadmium can be determined quantitatively in a medium consisting of ammonium tartrate-potassium nitrate (overall concentration 0.05-0.25 M) within pH range 7.0-9.0. In the actual procedure, an aliquot of cadmium solution was taken in a pyrex beaker containing 20 ml. of 0.1 M buffer and pH of the solution was adjusted at 8.0 by adding aqueous ammonia. The titrations were carried out at an applied potential of $-0.2V$ vs. SCE with the dropping mercury electrode. 2 ml. micro-burette was used to deliver the titrant in small portions and the galvanometer reading was noted initially as well as after each addition of the titrant. After the complete precipitation of cadmium, excess reagent gave the anodic diffusion current of its own resulting in a regular rise in the current. The plot of the volume of the reagent against galvanometer reading is shown in Fig. 1 (curve A). The results are given in Table 1.

Estimation of Copper and Cadmium in a Binary Mixture: An aliquot of a solution containing copper and cadmium was taken in a pyrex beaker containing the above buffer (0.1 M) of pH 8.0. The current was

noted at $-0.2V$ vs. SCE. As the addition of reagent continued, the diffusion current of copper reduced gradually and became steady. This intersection (Fig. 1, curve B) gave the end-point for copper. With

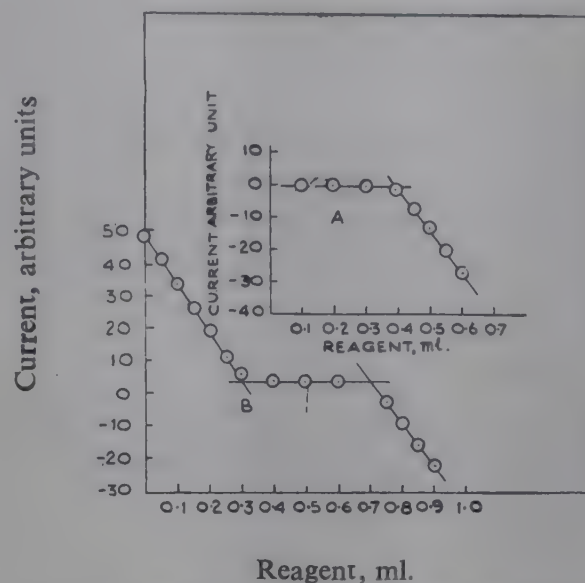


Fig. 1—Typical Amperometric Titration Curves.

TABLE 1—DETERMINATION OF CADMIUM WITH K-DITHIOTRIHYDROXYMETHYL AMINOMETHANE

Amount of Cd(II), mg.		% Error
Taken	Found	
0.2248	0.2247	—0.04
0.4496	0.4481	—0.33
1.1240	1.1240	—
1.6840	1.6840	—
2.2480	2.2340	—0.62

further addition of titrant, cadmium started getting precipitated and when whole of cadmium was removed excess of the reagent gave the anodic diffusion current of its own. The intersection at this point gave the end-point for cadmium. The results of these titrations are given in Table 2.

TABLE 2—DETERMINATION OF COPPER AND CADMIUM IN A MIXTURE

Amount Taken, mg.		Amount Found, mg.		% Error	
Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)
0.3813	1.5736	0.3812	1.5736	—0.03	—
0.7626	1.1240	0.7625	1.1240	—0.01	—
0.6355	0.8912	0.6353	0.9021	—0.03	—1.22
0.2542	1.3488	0.2569	1.3488	+1.06	—
0.3050	1.1140	0.3066	1.1180	+0.52	—0.36

Results and Discussion

The amperometric titration curves (Fig. 1) having a sharp break at the end-point occur at a stage when

metal : reagent ratio is 1 : 2. Considering the formula of the reagent and its structure it is reasonable to assume that in these reactions the cation replaces the potassium ion in the molecule and the complex has the formula $[(\text{CH}_2\text{OH})_3\text{C}-\text{NH}-\underset{\text{S}}{\overset{\parallel}{\text{C}}}-\text{S}]_2\text{M}$ where

M = cadmium or copper.

The data in (Tables 1 and 2) are reproducible and within limits of experimental errors. The procedure is very rapid and can be easily adopted. Easy synthesis of the reagent is the most noteworthy feature of this present investigation.

Acknowledgements

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Cation-complexing reagents have been investigated for their effect on the mobility of phosphates in soil columns. Citrate and EDTA salts were found to increase the mobility of phosphates tremendously; however, the EDTA salt was inferior to citrate. The movement of phosphate in presence of citrate in the soils followed the order: black soil > red soil > laterite soil used. Orthophosphate and pyrophosphate showed almost the same rate of penetration with both complexants which was higher than that of metaphosphate. The mobility of phosphate increased with an increase in the concentration of complexants.

Effect of Complexants on Migration of Phosphate In Soil Columns

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It has been observed that many anions, especially organic anions, decrease the activity of aluminium, iron and calcium in soils through chelation, forming stable complex or insoluble compounds and thus help in the release of soil phosphates. The organic anions, such as citrate, tartrate, oxalate and succinate, and inorganic anions, such as hydroxyl, fluoride and arsenate, have all been found to reduce phosphate fixation and thus help in the release of native and applied phosphate. Ferrocyanide, 8-hydroxyquinoline, humic acid, cupferon, aluminon, alizarin, tannin, EDTA and fulvic acid have also been found to prevent fixation of phosphate in soils. Though much work has been done on complexants, their effect on the migration of phosphate in Indian soils has not been studied.

The present study was undertaken to determine the effect of some complexants on the mobility of different phosphate ion species in three different types of soils under laboratory condition.

Experimental

Soil Column : The columns (Fig. 1) used for the present study were especially designed; their length was kept 13.2 cm. with 2.4 cm. internal diameter.

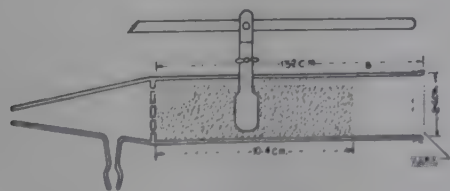


Fig. 1—Soil Column Assembly

These were provided with five holes at the bottom and slightly constricted at the lower end. These were clamped in iron stands.

Preparation of Soils : The following three soils were taken: laterite, red and black. As the soils did not possess uniform bulk density, they could not be packed accurately to the same height in the columns, so they were moistened with distilled water upto their moisture equivalent point, viz. 7.6 per cent for laterite, 8.0 per cent for red soil and 16.0 per cent for black soil. They were hand-kneaded in china clay dishes to obtain friable sample.

Packing of Soils : When the soils became friable, 125.0 g. of the samples were filled in the columns and carefully packed with a rubber thumper attached to one end with a long steel rod. They were packed to a height of 10.4 cm. in order to obtain an uniform bulk density. Afterwards, 5 ml. of distilled water was added to the soils in each column to moisten them with total moisture percentage of 11.6, 12.0 and 22.0 respectively.

The two complexants used, viz. sodium citrate and EDTA, were added before applying phosphates. The complexants were used in the aqueous form and at two concentrations, viz. equal to applied phosphorus and double this amount. The ortho, pyro and meta-phosphates were applied to soils packed in columns equivalent to their phosphate fixing capacity and also equivalent to twice this value as described by Langguth *et al.*¹ Thus, the amounts of phosphorus added

were 80 ppm KH_2PO_4 , 100 ppm $\text{K}_4\text{P}_2\text{O}_7$, and 120 ppm KPO_3 , and the concentration of complexants was equal to and double these values. The top of the soil columns were sealed with the help of tape in order to prevent the loss of moisture from the soils. The columns were allowed to remain at room temperature (30°C) for 7 days.

Separation of Soil Segments : After a lapse of 7 days the columns were dismantled. The soils were carefully extruded and cut into six segments (0-1.3, 1.3-2.6, 2.6-3.9, 3.9-5.2, 5.2-7.8 and 7.8-10.4 cm.) from the surface and segments were transferred into open dishes for drying in an oven. After drying, the soils were powdered and available phosphorus of each segment was determined by Olsen's method². The amount of various species of phosphate ions present in each segment was expressed as per cent of the total available phosphorus in the entire column of the soil, i.e.

% available phosphorus in each cut =

$$\frac{\text{Available phosphorus of each cut}}{\text{Total av. phosphorus of whole column}} \times 100$$

% available phosphorus of the applied phosphorus =

$$\frac{\text{Total available phosphorus of whole column}}{\text{Total amt. of phosphorus added in soil column}} \times 100$$

The criterion for choosing available phosphorus as an index of phosphorus migration was that the former has been reported to be one of the best methods for correlating chemically available phosphate with plant growth. The phosphate was invariably estimated according to the procedure given by Jackson³. The chemical properties of the soils (Table 1) were also determined by the procedure given in the above book³. The mechanical analysis of the soils was made following the International pipette method⁴. A control set was always maintained, wherever considered necessary. All experiments were done in duplicate and the average results have been given.

Experimental Results

The efficiency of complexants in releasing phosphorus in the soil columns is expressed in terms of available phosphorus present in any segment. It is observed that citrate is a more efficient complexant in mobilizing applied phosphorus to different layers than EDTA.

Effect of Citrate Anion : When citrate anion is used as the complexing agent for active phosphate fixers (sesquioxides) in soils, there was an increase in available phosphorus in all the three soils ranging from 60.0 per cent to 90.0 per cent of applied phosphorus when expressed as a sum of total available phosphorus in all the segments. From Fig. 2 it is

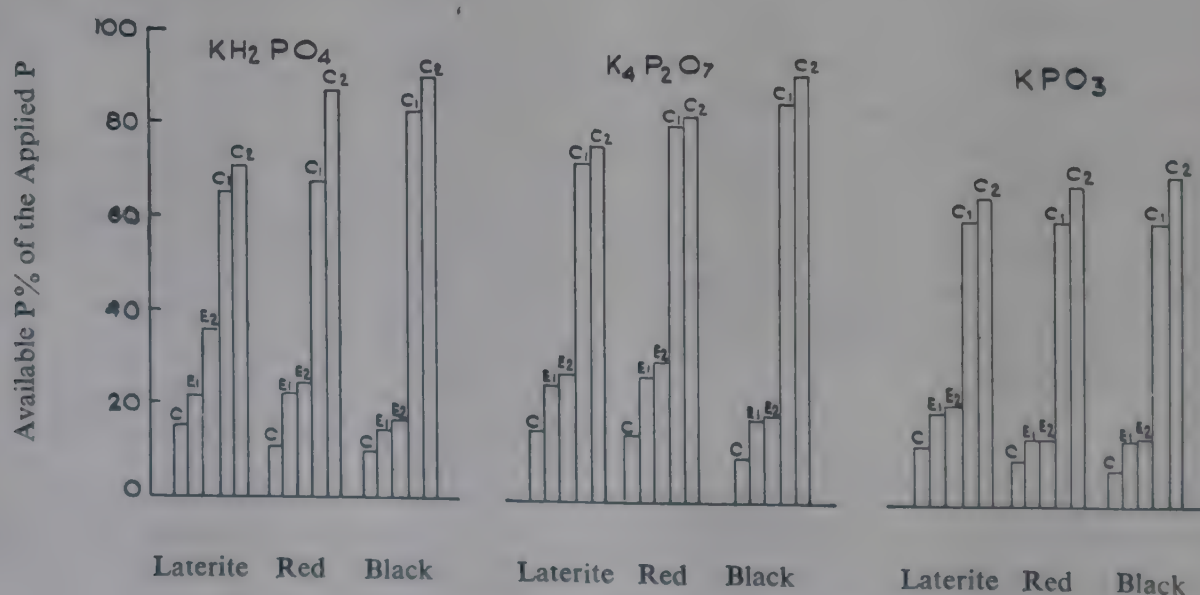


Fig. 2—Efficiency of Complexants in Mobilizing Phosphorus

Legend

- C — Control (Soil + Phos.)
- E₁ — P : EDTA 1 : 1
- E₂ — P : EDTA 1 : 2
- C₁ — P : Citrate 1 : 1
- C₂ — P : Citrate 1 : 2

evident that (a) efficiency of citrate anion in mobilizing applied phosphorus decreased in the order: black soil > red soil > laterite soil; (b) at higher dose of citrate anion the mobility of applied phosphorus increased in comparison to lower dose in all the soils; (c) the availability of applied phosphorus to soils followed the order: $\text{KH}_2\text{PO}_4 > \text{K}_4\text{P}_2\text{O}_7 > \text{KPO}_3$ in all soils.

TABLE 1—PROPERTIES OF SOILS USED IN PHOSPHATE MIGRATION STUDIES

Soil Properties	Laterite Soil*	Red Soil**	Black Soil†
pH	6.0	6.4	7.4
CaCO_3 %	—	0.44	2.5
Org. C, %	0.28	0.35	0.45
Total P_2O_5 , %	0.019	0.028	0.031
Available P_2O_5 , ppm	7.82	10.12	12.5
C.E.C.	7.5	2.9	35.0
Fe_2O_3 , %	8.5	4.64	5.39
Al_2O_3 , %	3.7	6.91	16.49
Clay, %	12.5	17.5	36.0
Silt, %	3.5	4.5	37.0
Coarse Sand, %	62.5	50.5	2.0
Fine Sand, %	21.50	27.5	25.0

* From Bhubaneswar (Orissa); ** From Meja (U.P.);

† From Gaipura (U.P.)

Effect of EDTA: An increase in available phosphorus ranging from 14.0 to 35.5 per cent was observed.

TABLE 2—EFFECT OF CITRATE ON THE DISTRIBUTION OF AVAILABLE PHOSPHORUS IN SOIL COLUMNS (AS PER CENT OF TOTAL AVAILABLE PHOSPHORUS)

Depth, cm.	Laterite Soil			Red Soil			Black Soil		
	Av. P % Control	P Complexant 1:1	Ratios 1:2	Av. P % Control	P Complexant 1:1	Ratios 1:2	Av. P % Control	P Complexant 1:1	Ratios 1:2
Phosphorus Source: KH_2PO_4									
0-1.3	23.0	16.6	5.5	23.5	19.5	15.0	35.5	23.0	10.5
1.3-2.6	19.0	16.6	4.0	26.5	16.5	13.0	26.5	23.0	10.5
2.6-3.9	27.5	16.6	2.0	24.5	9.5	10.5	23.5	23.0	19.0
3.9-5.2	23.5	16.6	29.5	15.5	9.5	9.5	9.0	23.0	19.5
5.2-7.8	5.5	16.6	29.5	8.0	22.5	26.0	6.0	5.0	19.5
7.8-10.4	2.0	17.0	29.5	2.0	22.5	26.0	Nil	3.0	21.0
Phosphorus Source: $\text{K}_4\text{P}_2\text{O}_7$									
0-1.3	26.0	14.5	8.5	25.5	10.5	9.0	39.0	15.5	8.5
1.3-2.6	26.0	14.5	5.5	29.5	12.5	9.0	25.0	17.0	10.0
2.6-3.9	30.0	15.5	10.0	30.5	16.5	14.5	22.0	17.0	12.5
3.9-5.2	11.0	15.5	14.0	13.5	21.5	16.5	8.0	20.5	20.5
5.2-7.8	5.0	20.0	31.0	1.0	26.0	24.0	6.0	23.0	24.0
7.8-10.4	2.0	20.0	31.0	Nil	13.0	27.0	Nil	7.0	24.5
Phosphorus Source: KPO_3									
0-1.3	35.0	13.5	7.5	41.0	10.0	5.5	49.5	10.0	4.0
1.3-2.6	35.0	13.5	7.0	36.0	13.5	8.0	34.9	16.5	12.0
2.6-3.9	20.0	16.0	9.0	14.0	14.5	15.5	14.0	17.5	18.5
3.9-5.2	8.0	17.0	16.5	9.0	22.5	16.5	2.0	17.0	18.5
5.2-7.8	2.0	20.0	29.5	Nil	25.5	24.5	Nil	19.0	20.0
7.8-10.4	Nil	20.0	30.5	Nil	14.0	30.0	Nil	20.0	27.0

(a) EDTA prevented phosphorus fixation in soils resulting in an increase in the available phosphorus in the following order: red soil > laterite soil > black soil.

(b) By increasing the dose of EDTA, only a little increase in available phosphorus was noticed.

(c) The available phosphorus from different phosphorus species was in the order: $\text{K}_4\text{P}_2\text{O}_7 > \text{KH}_2\text{PO}_4 > \text{KPO}_3$

Layerwise Distribution of Phosphate in Soil Columns: When citrate anion is used as a complexing agent, there is a tendency for phosphorus to migrate from top to bottom layers. Such an activity is further augmented at the higher level of citrate anion. It is interesting to note that the amount of phosphorus in the form of available phosphorus is mainly localized in 4th to 6th layer of each soil column. The behaviour of each phosphate ion species is almost same towards migration of phosphorus though differing in amount present in respective segments of soil columns. From Table 2, it is clear that there is no phosphorus in 5th and 6th layers of the soils with KPO_3 in control but on addition of citrate anion, a large amount of phosphorus is observed.

When EDTA is used as the complexing agent (Table 3), the migration of phosphorus from top to the bottom of soil columns is not so effective. However, there is a definite increase in the amount of

TABLE 3—EFFECT OF EDTA ON THE DISTRIBUTION OF AVAILABLE PHOSPHORUS IN SOIL COLUMNS (AS PER CENT OF THE TOTAL AVAILABLE PHOSPHORUS)

Depth. cm.	Laterite Soil			Red Soil			Black Soil		
	Av. P % Control	P Complexant 1:1	Ratios 1:2	Av. P % Control	P Complexant 1:1	Ratios 1:2	Av. P % Control	P Complexant 1:1	Ratios 1:2
Phosphorus Source : KH_2PO_4									
0-1.3	23.0	33.0	13.5	23.5	28.5	30.0	35.5	60.0	60.0
1.3-2.6	19.0	18.5	12.5	26.5	28.5	28.0	26.5	19.5	15.0
2.6-3.9	27.5	14.5	13.0	24.5	17.0	18.5	23.5	5.5	9.0
3.9-5.2	23.5	14.0	13.0	15.5	12.0	8.5	9.0	7.0	6.0
5.2-7.8	5.5	10.0	24.0	8.0	7.0	7.0	6.0	4.0	6.0
7.8-10.4	2.0	10.0	24.0	2.0	7.0	8.0	Nil	4.0	4.0
Phosphorus Source: $\text{K}_4\text{P}_2\text{O}_7$									
0-1.3	26.0	30.0	21.5	25.5	29.5	25.5	39.0	12.5	60.0
1.3-2.6	26.0	25.5	23.5	29.5	30.5	32.5	25.0	15.5	17.5
2.6-3.9	30.0	17.5	27.5	30.5	18.5	15.5	22.0	12.0	14.0
3.9-5.2	11.0	18.0	17.5	13.5	10.5	15.5	8.0	5.0	3.5
5.2-7.8	5.0	6.5	6.5	1.0	7.5	8.0	6.0	4.0	2.5
7.8-10.4	2.0	2.0	3.5	Nil	2.5	3.0	Nil	1.0	2.5
Phosphorus Source: KPO_3									
0-1.3	35.0	41.5	36.5	41.0	45.0	39.5	49.5	48.5	45.0
1.3-2.6	35.0	40.0	35.5	36.0	30.0	32.5	34.5	30.5	28.5
2.6-3.9	20.0	11.0	17.5	14.0	12.0	15.0	14.0	17.5	20.5
3.9-5.2	8.0	5.5	6.5	9.0	10.0	9.0	2.0	3.5	5.0
5.2-7.8	2.0	1.0	3.0	Nil	3.0	4.0	Nil	Nil	1.0
7.8-10.4	Nil	1.0	1.0	Nil	Nil	Nil	Nil	Nil	Nil

TABLE 4—EFFICIENCY OF COMPLEXANTS IN RELEASING PHOSPHORUS IN SOIL COLUMNS AFTER 7 DAYS (AS AVERAGE PHOSPHORUS % OF APPLIED PHOSPHATE)

(For all the segments on average)

Source of Phosphorus	Av.P, % (C)	Laterite Soil		Av.P, % (C)	Red Soil		Av.P, % (C)	Black Soil	
		1:1	1:2		1:1	1:2		1:1	1:2
(A) Sodium Citrate									
KH ₂ PO ₄	14.5	65.5	70.8	11.0	67.5	87.0	10.5	83.0	90.0
K ₄ P ₂ O ₇	15.0	72.0	76.0	14.0	80.0	81.0	9.5	85.0	91.0
KPO ₃	13.0	60.5	65.5	10.0	60.0	67.0	8.0	60.5	70.0
(B) EDTA									
KH ₂ PO ₄	14.5	21.5	35.5	11.0	22.5	24.0	10.5	15.0	16.5
K ₄ P ₂ O ₇	15.0	25.0	27.0	14.0	27.5	30.0	9.5	18.0	19.0
KPO ₃	13.0	20.0	21.0	10.0	21.0	21.0	8.0	14.0	14.5

C = Control, 1:1 and 1:2 denote P: Complexant ratios.

phosphorus over control at the bottom of the column. The localization of phosphorus was found mainly in 3rd and 4th layer with KH_2PO_4 and $\text{K}_4\text{P}_2\text{O}_7$ but with KPO_3 there was no migration of phosphorus to the bottom layers.

Discussion

When phosphate fertilizers are added to the soil along with the different complexants there is a competition between phosphate anions and the complexants to react with iron, aluminium and calcium. As the complexants have a greater affinity for certain of

the soil constituents, the complex iron, aluminium and calcium of soils and thus reduce the possibility of phosphate ions to be held up by sesquioxides. This results in reduced fixation of phosphorus by soils and increased mobility of phosphorus to the lower layers in the soil columns.

In the present investigation, the efficiency of citrate anion was found to be greater than EDTA with all species of phosphate ions. It is well-known that citrate anion has a chelating power for both iron and aluminium, thus increasing the available phosphate to a great extent which in turn is responsible for the

migration of phosphorus throughout the soil column. Similar results have been reported by Satchell⁵.

The effect of EDTA was found quite low. It is known that EDTA chelates iron, aluminium and calcium simultaneously. It has been further reported that the complexant which chelates more than two constituents of a soil simultaneously, generally exhibits a poor effect in decreasing phosphate fixation⁶. Hence, the mobility of phosphate in presence of EDTA is low. The complexants used have the ability to mobilize pyro-and metaphosphates like orthophosphates.

The distribution of available phosphorus in different segments may be taken as an index of phosphorus mobility. The tendency of phosphorus to move to greater depths in presence of complexants clearly

shows that the complexants have helped in the migration of phosphorus from the upper to lower layers. The citric acid is more effective than EDTA in mobilizing applied phosphorus.

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Rhizosphere mycoflora of healthy and diseased plants of *Pennisetum typhoides* (Burm f.) Stapf and Hubb. has been studied. The fungal population of healthy plants generally exceeded the diseased ones. Aspergilli outnumbered throughout the course of this investigation. Amino acids and sugars obtained were always higher in quality and quantity in healthy plants. The root leakage seems to play an important role in the colonization of various fungi in rhizosphere of healthy and diseased plants of *Pennisetum typhoides*.

Investigations into Rhizosphere Mycoflora Part 8—Fungal Population of Diseased and Healthy Plants of *Pennisetum Typhoides* (Burm f.) Stapf & Hubb

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Introduction

The rhizosphere fungal population, greatly affected by plant condition, has been reported by several workers¹⁻⁸. Sadasivan⁹, Mishra and Kamal¹⁰ and Sivaneson and Manners¹¹ reported considerable differences in the rhizosphere fungal population of healthy and diseased plants. The studies have, however, been concerned either with the virus-infected plants⁹⁻¹² or to wilt diseases.^{7, 11, 13, 14} No proper attention has been paid to investigate the changes in rhizosphere mycoflora when aerial parts of the plants are infected by fungal pathogens and this has been worked out in the present investigation.

Experimental

The healthy(H) and diseased(D) plants of *Pennisetum typhoides* (Burm f.) Stapf & Hubb., raised in the experimental plot in the campus of the University of Gorakhpur, were selected for the present study. The leaves and fists of diseased plants were badly damaged by *Puccinia Penniseti*, *Tolyposporium peniculariae* and in a few cases by *Sclerospora graminicola*. First, sampling was done when plants aged 60 days. Subsequent samplings were carried out at the interval of 20 days. Roots and non-rhizosphere soils, aseptically collected (as described by Srivastava¹) in sterilized containers using a sterilized spatula, were brought to the laboratory. The fungal flora of rhizosphere and non-rhizosphere regions was assessed by method

adopted by Mishra and Kanaujia¹⁵. The moisture content of the soil was determined by the method suggested by Piper¹⁶ and pH was determined by electric pH meter. The fungal population was calculated on the dry weight basis of the soil.

The extracts of healthy and diseased roots of *P. typhoides* was prepared as described by Kanaujia¹⁷. This was then analysed for the presence of amino acids and sugars^{18, 19} by unidirectional paper chromatography. The amount of free amino acids was also known with the help of densitometer.

Results

The 26, 28 and 21 fungal isolates were recorded from the rhizosphere of healthy and diseased plants and from non-rhizosphere respectively. The details are furnished in Table 1. Qualitatively, aspergilli outnumbered throughout the course of this investigation whereas *Cladesporium* dominated in all the three sets. The distribution pattern of the number of fungal species was very regular on different stages of the plants. The highest and the lowest numbers of species were always recorded from non-rhizosphere and rhizosphere of diseased plants respectively except at the senescent stage where the fungi were higher in the D set (Table 2).

The fungal population per g. dry soil in healthy set always exceeded the diseased one. The maximum

TABLE 1—RHIZOSPHERE MYCOFLORA OF DISEASED AND HEALTHY PLANTS OF *P. Typhoides* AND NONRHIZOSPHERE SOIL

Fungal Species	Healthy	Diseased	Nonrhizosphere
<i>Rhizopus nigricans</i>	p	p	p
<i>R. stolonifer</i>			p
<i>Mucorehiemalis</i>	p	p	p
<i>M. racemosus</i>			p
<i>Mucor sp.</i>	p	p	
<i>Syncephalastrum racemosum</i>	p		
<i>Chaetomium globosum</i>	p		
<i>Phoma hibernica</i>	p		
<i>Botryodiplodia theobromae</i>	p		
<i>Monilia sitophila</i>	p	p	p
<i>Trichoderma viride</i>	p	p	p
<i>Aspergillus nidulans</i>	p	p	
<i>A. fumigatus</i>	p	p	p
<i>A. flavus</i>	p	p	p
<i>A. terreus</i>	p	p	p
<i>A. flavipes</i>	p	p	p
<i>A. ustus</i> (gp.)			p
<i>A. niger</i>	p	p	p
<i>A. aculeatus</i>	p	p	p
<i>A. ochraceous</i>		p	p
<i>A. sulphureus</i>		p	
<i>A. versicolor</i>	p		
<i>A. fischeri</i>	p	p	
<i>A. gorakhpurensis</i>	p	p	
<i>A. sydowi</i>			p
<i>Penicillium expansum</i>	p	p	
<i>P. chrysogenum</i>	p	p	
<i>Cladosporium herbarum</i>	pp	pp	pp
<i>C. epiphyllum</i>		p	p
<i>Verticillium albo-atrum</i>	p	p	
<i>Curvularia tetramera</i>	p	p	p
<i>C. lunata</i>	p	p	p
<i>C. geniculata</i>		p	
<i>Helminthosporium sativum</i>		p	
<i>Fusarium moniliforme</i>	p	p	
<i>F. nivale</i>	p	p	p
White sterile colonies	p	p	p
No. of Species	26	28	21

p—indicates presence; pp—indicates dominant by presence; Gaps indicate absence.

TABLE 2—DISTRIBUTION OF NUMBER OF FUNGAL SPECIES IN THE RHIZOSPHERE OF HEALTHY AND DISEASED *P. Typhoides* AND IN NONRHIZOSPHERE AT DIFFERENT STAGES

Stage	Rhizospheres		Nonrhizosphere
	H	D	
1. Pre.flowering	15	11	17
2. Flowering	13	10	16
3. Post-flowering	17	14	19
4. Senescence	13	17	16

H=Healthy, D=Diseased set.

and the minimum population in the rhizosphere of healthy plants was noticed at flowering and pre-flowering stages. After flowering, it decreased gradually during post-flowering and senescent stages. In diseased set, however, the population gradually increased from pre-flowering to the senescence where it was maximum (Fig. 1). Differences in the rhizosphere population in H and D plants were considerably more at the pre-flowering, while in the subsequent stages it decreased gradually (Fig. 1). Non-rhizosphere population also increased continuously and was highest at the end of the experiment. The population in NR was always lower than corresponding rhizosphere sets (Fig. 1).

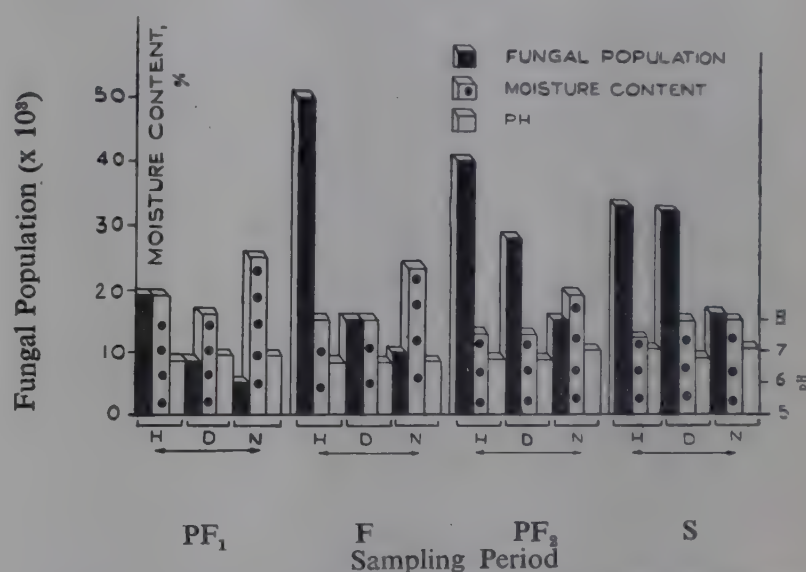


Fig 1—Distribution of Rhizosphere and Non-rhizosphere Fungal Flora at Different Stages of Healthy and Diseased Plants of *Pennisetum Typhoides* (PF₁—Preflowering; F—Flowering; PF₂—Post-flowering; S—Senescence)

H-Healthy Set } Rhizosphere N-Nonrhizosphere
D-Diseased Set }

The moisture content of the rhizosphere and non-rhizosphere soil samples was higher at preflowering, exhibited increasing tendency at the subsequent stages, except in diseased set where an increase was noticed at senescence. No appreciable difference in the pH of NR and diseased set samples was observed, however, in H set it varied in between 6.7 and 7.1 with an increasing tendency from preflowering to senescent stages (Fig. 1).

Eleven and nine amino acids were detected from the root extracts of H and D sets respectively. Except thyronine and an unidentified amino acid 'A' (Rf= 0.74) (which were present in healthy roots only) remaining were of common occurrence. The amount of individual acids was always more in H and D roots (Table 3). Extracts analysed for sugars yields 7 and 6 number of species (Tables 1 and 2 and Fig. 1). The

nose present in the H roots was not detected from the D ones (Table 4).

TABLE 3—DISTRIBUTION OF AMINO ACIDS IN THE ROOT EXTRACT OF HEALTHY (H) AND DISEASED (D) PLANTS OF *P. Typhoides* AT DIFFERENT STAGES, UG./2G. OF FRESH ROOTS

Amino Acids	Pre-flowering		Flowering		Post-flowering		Senescence	
	H	D	H	D	H	D	H	D
Alanine	625	—	716	212	214	206	—	—
Cystein	250	174	314	204	211	206	192	184
Glycine	200	—	219	—	178	92	118	—
Iso-leusine	2425	1948	2609	1804	1752	1622	1664	1512
Phenylalnine	571	—	618	319	308	—	—	—
Tyrosine	463	306	217	318	—	—	—	—
Thyronine	509	—	812	—	426	—	—	—
Valine	—	—	419	—	243	180	142	152
Unidentified 'A' (0.74)	+	—	+	—	—	—	—	—
Unidentified 'B' (0.88)	+	+	+	+	+	+	+	+
Unidentified 'C' (0.78)	+	—	+	—	—	+	—	—
No. of Amino Acids	10	4	11	6	8	7	5	4
+ = present — = absent								

TABLE 4—DISTRIBUTION OF THE SUGARS IN THE ROOT EXTRACT OF HEALTHY (H) AND DISEASED (D) *P. Typhoides* AT DIFFERENT STAGES

Sugars	Pre-flowering		Flowering		Post-flowering		Senescence	
	H	D	H	D	H	D	H	D
Arabinose	+	—	+	+	+	—	+	—
Glucose	+	+	+	+	+	+	+	+
Maltose	+	+	+	+	+	—	—	—
Rhamnose	—	—	+	—	+	—	—	—
Sucrose	+	+	+	+	+	+	+	+
Xylose	+	+	+	+	+	+	+	—
Unidentified (Rg. 25)	—	—	+	+	—	—	—	—
No. of sugars	5	4	7	6	6	3	4	2
+ = present — = absent								

Discussion

The rhizosphere population is greatly affected by the root exudation ^{2-4, 1, 17}. As evident from Tables 3 and 4, the amino acids and sugars were always comparatively higher in the root extracts of healthy plants than in the diseased ones. Quantitatively also, the amino acids being appreciably more at the preflowering and flowering stages decreased at post-flowering and senescence. The variation, however, in the quality and quantity of amino acids and in the quality of the sugars possibly accounted for the differences

in the fungal population of H and D sets (Srivastava¹). These root components affected the rhizosphere population directly. The condition in the diseased plants is slightly different where due to severe foliar infection the photosynthetic activity of the plants is reduced manifold which in turn renders the poor growth of the plants. The poorly developed roots of this set contained lesser amino acids and sugars (Tables 3 and 4) which possibly resulted in the poor exudation of nutrients and therefore, low population at early stages in this set is admissible. During post-flowering and senescent stages, the diseased set supported higher fungal population and also the greater number of species (Tables 1 and 2 and Fig. 1). The diseased plants started dying earlier. Some of the roots got decomposed much earlier than the healthy plants. Thus, the condition of the diseased set is different where in addition to exudation by living roots, some of the dead and decomposed roots also accounted for the increased rhizosphere fungal population at preflowering and senescent stages. In healthy set, on the other hand, exudation played the major role particularly at preflowering and flowering stages, where higher population was recorded; thereafter, at post-flowering and senescence with decrease in exudation and delayed root decomposition as compared to diseased set, population also decreased.

The sharing of the majority of species by both H and D sets (Table 1) may be ascribed to the similarity in the amino acids and sugars of the plants. The restricted distribution of several species (Table 1) in the rhizospheres of two plants is possibly due to the some differences in the root exudates and the antagonism amongst the large number of fungal species.

A few non-rhizosphere fungal failed to establish in either of the rhizospheres; for this the possibility of release of some harmful substances by roots may also not be overlooked²⁰.

More information may, however, be obtained if the rhizosphere microfungi were studied in relation to their nutritional liking for the individual amino acids and sugars. This will be helpful in understanding the preferential liking of the organisms for the nutrients exuded by the roots which will ultimately regulate the growth of the selected forms in the rhizosphere region.

With variation in root exudate in relation to time and space the rhizosphere fungal population varies. The information so far available is, however, quantitative. The present study also does not throw much

light on this aspect and mostly correlates the quantity of the fungal flora in relation to amino acids and sugars. Effort is, however, being made to investigate this aspect which will be published later.

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The effect of soil and foliar applied phosphorus on the yield and protein content of soyabean in two acid soils was studied under greenhouse condition. On Onverwagt clay soil, a superior effect of phosphorus applied on the leaves as compared to its direct addition on the soil was observed. On Inki clay soil, the effect of phosphorus applied on the leaves was only significant. The addition of phosphorus was beneficial in increasing the protein content of the grain on both the soils. The effect of treatments on protein was significant on the Onverwagt soil but not on Inki soil.

Soil and Foliar Fertilization of Phosphorus on Yield and Protein Content of Soyabeans (*Glycine max.* L. merr.)

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There are several studies to show that yield of soyabeans is increased on fertilization with phosphorus¹⁻⁵. However, the response to phosphorus was not always consistent. In Guyana, a beneficial effect to application of phosphorus was noted on one soil⁶, but a significant effect could not be observed on other two soils⁷. The soils under investigation were highly acidic and had a strong tendency to fix phosphates. Their available phosphorus content was low. One of the possible reasons which would have negated a response under these soil conditions might be the fixation of applied phosphorus. The leaching of phosphorus under high rainfall conditions may also contribute to the loss of this plant nutrient.

The soil conditions do not limit the availability of the fertilizers when these are applied to the foliage. Several research workers have found a beneficial effect on crops due to foliar fertilization⁸⁻¹². It has also been claimed that plant nutrients applied through leaves have a superior effect in comparison to their direct addition to soil^{9, 12}. De and Singh¹¹ found that in foliar application one-fifth to one-fourth of the usual quantity of nutrient was as effective as the full dose in direct soil application.

In view of the fact that soil fixation might have interfered with the response of phosphorus in field experiments carried out earlier⁷, the present investigations were carried out to compare the effect of phosphorus applied on the soil to that on the leaves. In

order to eliminate the leaching losses, the experiment was done under greenhouse condition.

Materials and Method

The experiment was conducted in the greenhouse on two clay soils, viz. Onverwagt and Inki, collected from the Central Agricultural Station (C.A.S.) and the Central Horticultural Station (C.H.S.) respectively. The Onverwagt soil is composed of marine sediments, while the Inki soil has formed from riverine deposits. The physico-chemical properties of the top 15 cm. soils are given in Table 1.

The surface soils were air-dried, crushed and passed through a 5 mm. sieve. 5 kg. of screened soils were filled in near-cylindrical polythene pots (30 × 22 cm.), which had perforated bottoms resting on shallow plastic dishes. These dishes retained any water which tended to drain out. The following treatments were made on each of the two soils: (1) Control, (2) 15 kg. P/ha. on soil as well as on leaves, (3) 30 kg. P/ha. on soil as well as on leaves. The pots were arranged in a randomized block design with four replications on each soil. The soils in the pots were maintained at field capacity moisture throughout the period of crop growth. After moistening the pots, three pregerminated seeds of variety 240664 were planted in each pot. After the emergence of shoot,

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TABLE 1—SOME CHEMICAL AND PHYSICAL PROPERTIES OF THE TOP 15 CM. OF THE EXPERIMENTAL SOILS

Location	Soil Type	pH	Org. C, %	Total N, %	Av. P, ppm	Mechanical Analysis			Exchangeable Cations		
						Sand, %	Clay, %	Silt, %	meq. 100 g. soil		
									Ex. K	Ex Ca	Ex. Mg
C.A.S.	Onverwagt Clay	5.8	1.4	0.28	6	10	54	36	0.45	6.9	9.9
C.H.S.	Inki Clay	5.2	1.5	0.20	1	7	58	35	0.41	6.7	6.5

fertilizer phosphorus was applied after a period of 40 days, when a canopy of foliage had formed. The leaves were sprayed with a 1.6 per cent solution of triple superphosphate in the form of a fine mist, delivered from a hand sprayer. Two more sprays were made, each after an interval of one week. The total volume of the spray made in each treatment was so calculated as to deliver an exact amount of phosphorus fertilizer. The spray fertilization was done before the soyabean bloomed. After the third spray was made, a few leaf spots had appeared as a result of scorching. The yield of oven-dried (110°C) soyabean grains was taken. The grain protein was determined by estimating the total nitrogen by the microkjeldahl method¹³ and multiplying the nitrogen content with a factor of 6.25.

Results and Discussion

(a) *Yield*: The yield of soyabean per pot as effected by two levels of phosphate fertilizer applied to the soil and foliage is given in Table 2.

TABLE 2—THE YIELD OF SOYABEAN SEEDS IN ONVERWAGT CLAY AND INKI CLAY SOILS, G./POT

Serial No.	Treatment	Onverwagt Clay Soil	Inki Clay Soil
1	Control	11.60 a	14.40 a
2	15 kg P/ha on soil	15.10 b	17.15 ab
3	15 kg P/ha on leaves	18.17 b	20.05 b
4	30 kg P/ha on soil	15.15 b	17.30 ab
5	30 kg P/ha on leaves	16.42 b	19.33 b

* Treatments followed by the same letter are not significantly different from each other according to Duncan's multiple range test.

The results obtained on Onverwagt clay soil revealed that all phosphorus treatments whether applied

to the soil or foliage increased the soyabean yield significantly. The combined effect of all the treatments was highly significant ($F=5.68$). The treatment differences between the foliage applied fertilizer and control were significant at 1 per cent level. In contrast the effect of soil applied phosphorus was significant at 5 per cent. On the Inki soil, the phosphate fertilizer treatments increased the grain yield significantly ($F=4.96$). The differences between foliage applied phosphorus and control treatments were significant only. The differences in the soil applied fertilizer to control were non significant.

Thus, on Onverwagt soil, a superior effect of phosphorus applied on to leaves as compared to its direct addition on soil was observed. On Inki soil, the treatment differences between foliage applied and control treatments were only significant. On this soil, the differences between soil applied fertilizer and control were non-significant. As the experiments on both the soils were carried out under identical conditions and the leaching losses were practically nil, it appears that certain soil factors interfered with the availability of phosphate fertilizer added to the soil. Jacquinet¹⁴ found that clay soils showing no response to phosphate fertilizing had a strong phosphate-fixing capacity. Khan and Chowdhury¹⁵ noted that 88 per cent of the phosphorus added as triple superphosphate was retained by an acid clay soil. In Philippines, soils with high phosphate adsorbing capacity released no available phosphorus even after heavy treatment with superphosphate¹⁶. In Guyana, phosphorus fixation was high on many soils¹⁷.

(b) *Protein*: The data on the influence of the method of phosphate application on protein content of soyabean are given in Table 3. On the Onverwagt soil, all the phosphorus treatments, whether phosphorus was applied to the soil or to the foliage increased the protein content of soyabean ($F=365.4$). All the treatment differences were significant. On

the Inki soil, the effect of treatments on protein content was found non-significant ($F=1.31$). However, all the phosphorus treatments increased the protein content of soyabean as compared to control.

TABLE 3—EFFECT OF PHOSPHATES ON PERCENTAGE PROTEIN OF SOYABEANS ON ONVERWAGT CLAY AND INKI CLAY SOILS

Serial No.	Treatment	Onverwagt Clay Soil	Inki Clay Soil
1	Control	31.25 a	30.70 a
2	15 kg. P/ha. on soil	37.25 b	33.25 a
3	15 kg. P/ha. on leaves	32.90 c	32.03 a
4	30 kg. P/ha. on soil	34.70 d	32.88 a
5	30 kg. P/ha. on leaves	30.68 e	34.88 a

* Treatments followed by the same letter are not significantly different from each other according to Duncans' multiple range test.

There is a close relationship between the phosphorus and nitrogen metabolism in the plants. The nitrogen metabolism was affected at the amide stage in phosphorus-deficient plants, leading to amide nitrogen accumulation and poor protein formation¹⁸. A severe phosphorus deficiency caused decomposition of protein synthesized previously and movement of amino acids into the leaves¹⁹. Pliskova²⁰ noted that fixation of atmospheric nitrogen by crop and amino acid contents of the bleeding sap depended on the phosphorus level in the nutrient medium. Plants grown with a lower level of phosphorus showed nitrogen deficiency. It is reasonable to assume that in the present experiment, application of phosphorus

and its increased uptake would have resulted in an increase in soyabean protein.

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The amounts of basic sites and strength on the surfaces of alumina-zirconia ($\text{Al}_2\text{O}_3\text{-ZrO}_2$), silica-zirconia ($\text{SiO}_2\text{-ZrO}_2$)—heat-treated at various temperatures—alumina-thoria ($\text{Al}_2\text{O}_3\text{-ThO}_2$), silica-thoria ($\text{SiO}_2\text{-ThO}_2$), alumina-molybdenum trioxide ($\text{Al}_2\text{O}_3\text{-MoO}_3$), alumina-tungsten trioxide ($\text{Al}_2\text{O}_3\text{-WO}_3$), silica-molybdenum trioxide ($\text{SiO}_2\text{-MoO}_3$) and silica-tungsten trioxide ($\text{SiO}_2\text{-WO}_3$) were determined by acid adsorption technique using several acids in the range of $\text{pK}_a=0.64$ to 9.9. It is observed that zirconia and thoria supported on silica and alumina have strong basic sites at $\text{pK}_a=9.9$, while molybdenum trioxide and tungsten trioxide supported on silica and alumina have weak and medium basic sites at $\text{pK}_a=0.64$ to 4.41. The basicity and surface area decrease with the rise in calcination temperature.

It has been found that the catalytic activity of various mixed oxides for decomposition of hydrogen peroxide correlates well with the basicities at $\text{pK}_a \geq 10$.

Basic Property and Catalytic Activity of Some Solid Surfaces

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The knowledge of the basic sites and base strength of the catalysts is necessary to understand the performance and predict the activity of the catalyst. Boehm¹ has recently reported the basic properties of hydroxylated metal oxide surfaces by several acid adsorption techniques. Tanabe *et al.*^{2,3} have determined the basicity and base strength of several alkaline-earth oxides and correlated the values of basicity with catalytic activity. Recently, the present authors have also observed a relation between basic property and catalytic activity while studying cleavage of aromatic ethers by hydrochloric acid in non-aqueous media in presence of several metal oxide catalysts⁴⁻⁶. In order to elucidate the nature of active centres on mixed oxide surface, the changes in surface area and basic properties with change of calcination temperature have been studied. In the light of the observed surface basic properties, the catalytic activity of these mixed oxides for the decomposition of hydrogen peroxide has been discussed.

Experimental

Catalysts and Reagents : The mixed oxide catalysts were prepared by the precipitation and impregnation technique as described earlier^{7,8}. Merck's quality hydrogen peroxide which was purified by distillation at reduced pressure was used in this investigation. All the other chemicals used in this work were guaranteed reagents.

Measurement of Basic Property : The technique adopted was essentially the same as described earlier⁵ by the present authors. The basicity of mixed oxides calcined at various temperatures was measured by back-titrating the excess of the trichloroacetic acid with a base. For this purpose, 1 g. of the catalyst was suspended in 50 ml. solution of 0.05 M trichloroacetic acid in dry benzene. The mixture was agitated for two hours and then kept aside for 24 hours. 5 ml. of the supernatant solution was titrated against 0.025M *n*-butylamine in dry benzene using bromothymol blue as indicator. The basicity of the mixed oxide was calculated readily from the decrease in trichloroacetic acid concentration in benzene. Similarly, the base strength of these mixed oxides was determined by acid adsorption technique using comparatively weaker acids, such as chloroacetic acid ($\text{pK}_a = 2.66$); acetic acid ($\text{pK}_a = 4.41$); and phenol ($\text{pK}_a = 9.9$), and the values of basicity are presented in Tables 1 and 2. In some experiments, 0.05M caustic soda (free from carbon dioxide) was used as titrating base in case of some of the weaker acids.

Surface Area : The surface areas of the heat-treated samples of different mixed oxides were measured by liquid adsorption method using EGME technique of Heilman and Carter⁹.

Kinetic Measurements : The decomposition of hydrogen peroxide was followed titrimetrically. A

known weight of the catalyst was taken in a conical flask and inserted in a thermostat. 100 ml. of hydrogen peroxide solution (0.2M) in double-distilled water and the reaction vessel with 1 g. of catalyst were placed in a thermostat at 30°C for sufficient time to attain the ambient temperature and then mixed together. The contents in the flask were stirred uniformly. At suitable time intervals, a known amount of undecomposed hydrogen peroxide was withdrawn and rapidly added to 5 ml. of 2N ice-cold sulphuric acid and immediately titrated with 0.01N potassium permanganate.

Since the present catalysts have both acidic as well as basic centres on their surface and that both these catalyse the decomposition of hydrogen peroxide, an attempt has been made to evaluate the amount of decomposition brought about by basic sites¹⁰ by poisoning the acidic sites with neutral red ($pK_a=6.8$)

Results and Discussion

The results of basicity measurements at various base strengths of alumina-zirconia, silica-zirconia and oxides of MoO_3 , WO_3 , ThO_2 supported on silica and alumina are given in Tables 1 and 2. An examination of these results (Tables 1 and 2) indicates that the basicity and base strength distribution change remarkably with the rise in temperature of heat treatment. In Fig. 1 is shown the plot of pK_a values of acids used for adsorption studies against the total basicity (meq./g.), for alumina-zirconia catalyst heat treated at various temperatures. A similar plot was obtained for silica-zirconia catalyst. The base strength of the surface increase as the pK_a value of acid increases. It is observed from Fig. 1 for alumina-zirconia catalyst, that the basicity and base strength stronger than $pK_a = 9.9$ appear on the surface heat-treated at 120-800°C. In the case of silica-zirconia (Table 2)

the strong basic sites at $pK_a = 9.9$ appear on the surface when heat treated at 120-500°C and those at medium and weak basic strength at $pK_a=0.64$ to 4.41 appear at 120-720°C. It is observed in case of molybdenum trioxide and tungsten trioxide supported on silica and alumina that they have no strong basic sites at $pK_a=9.9$ but have number of weak basic centres at $pK_a=0.64$ to 4.41. ThO_2 supported on silica and alumina has strong basic centres at $pK_a=9.9$. From these results it is observed that basicity at various base strength decrease in the following order: alumina-zirconia > alumina-thoria > silica-thoria > silica-zirconia.

The values obtained by the phenol adsorption are generally lower than the values obtained by other acids. This is because of the fact that other acids are strong ($pK_a = 0.64 \sim 4.4$) and are able to measure even weak basic sites whereas phenol is a weaker acid ($pK_a=9.9$) and measures only strong basic sites.

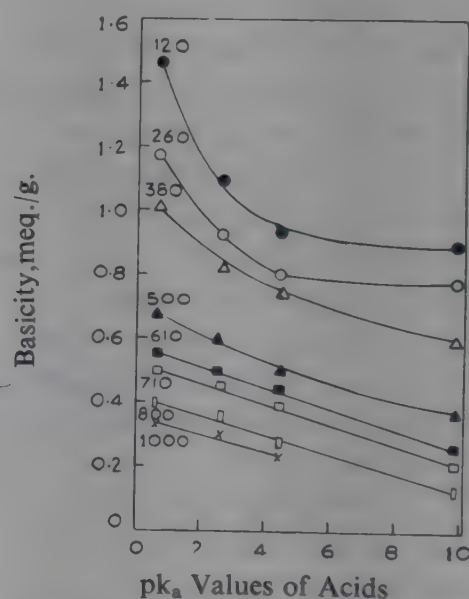


Fig. 1—Basicity and Base Strength of Alumina-Zirconia Catalyst Calcined at Various Temperatures.

TABLE 1—BASICITY AND BASE STRENGTH DISTRIBUTION OF ALUMINA-ZIRCONIA (80%-20%) CATALYST

Temp. of Calcination, °C	Surface Area, m ² /g.	Basicity Calculated from Adsorption of Acids, meq./g.				Decomposition of H_2O_2 , $k \times 10^3$ hr ⁻¹ g. ⁻¹
		$pK_a=0.64$	$pK_a=2.66$	$pK_a=4.41$	$pK_a=9.9$	
120	158.9	1.470	1.112	0.942	0.900	24.0
260	135.0	1.180	0.932	0.802	0.780	21.0
380	122.9	1.020	0.836	0.751	0.600	16.0
500	98.9	0.680	0.608	0.504	0.380	10.0
610	75.0	0.560	0.504	0.456	0.260	6.9
710	65.0	0.500	0.464	0.401	0.208	4.8
800	50.0	0.400	0.362	0.284	0.120	2.6
1000	22.9	0.340	0.308	0.246	—	—

TABLE 2—BASICITY AND BASE STRENGTH DISTRIBUTION OF SOME MIXED OXIDE CATALYSTS

Catalyst	Temp. of Calcination, °C	Surface Area, m ² /g.	Basicity Calculated from Adsorption of Acids, meq./g.				Decomposition of H ₂ O ₂ , k × 10 ² hr ⁻¹ g. ⁻¹
			pK _a =0.64	pK _a =2.66	pK _a =4.41	pK _a =9.9	
SiO ₂ -ZrO ₂ (89%-11%)	120	509	1.30	0.764	0.597	0.24	6.82
	240	441	1.11	0.714	0.542	0.21	5.54
	320	440	0.96	0.646	0.488	0.14	3.78
	420	435	0.80	0.574	0.462	0.12	2.86
	500	408	0.58	0.488	0.400	0.10	1.84
	610	355	0.48	0.389	0.320	Nil	—
	720	326	0.36	0.322	0.268	Nil	—
SiO ₂ -ThO ₂ (85%-15%)	400	355	1.0	0.542	0.408	0.30	8.06
Al ₂ O ₃ -ThO ₂ (72%-28%)	450	46.8	1.0	0.724	0.648	0.60	16.24
SiO ₂ -MoO ₃ (81%-19%)	450	298	0.35	0.286	0.246	Nil	—
Al ₂ O ₃ -MoO ₃ (74%-26%)	450	82.2	0.30	0.268	0.230	Nil	—
SiO ₂ -WO ₃ (84%-16%)	400	281.8	0.35	0.274	0.262	Nil	—
Al ₂ O ₃ -WO ₃ (84%-16%)	400	83.2	0.40	0.384	0.345	Nil	—

In Fig. 2 is given the plot of basicity (meq./g.) at various base strength against the temperature of calcination for alumina-zirconia catalyst. A similar plot was obtained for SiO₂-ZrO₂ catalyst. It is observed from Fig. 2 and also Table 2, that the basicity at various base strength decreases with the rise in temperature of heat treatment. Boehm¹, Yamadaya *et al*¹¹ and Peri¹² have attributed their observed basic property of several metal oxides as due to the adsorbed hydroxyl (OH) groups present on the surface. In the present work the decrease in basicity with the rise in the calcination temperature is probably due to the removal of hydroxyl groups present on the surface as water molecule. With still further rise in temperature of heat treatment, there are no hydroxyl groups

to be lost as water molecules, structural changes take place on the surface which reduce the surface area which is evident from the values of surface area presented in Tables 1 and 2 and this accounts for reduction in surface basicity. This conclusion supports the views of Hindin and Weller¹³ in the dehydration of alumina.

Correlation of Basic Property with Catalytic Activity: The values of the first order rate constant *k* of the mixed oxides calcined at various temperatures for decomposition of hydrogen peroxide reaction are given in the last columns of Tables 1 and 2. It is observed that a good correlation exists between basicity measured by phenol adsorption method and catalytic activity (first order rate constant *k*). Both phenol and hydrogen peroxide have a pK_a value in the range¹⁴ 9 to 11 and are nearly the same, and the basicity values measured by phenol adsorption are catalytically active in the decomposition of hydrogen peroxide. The basicity values measured by other strong acids (pK_a=0.64 to 4.41) are high and do not correlate with the catalytic activity as these acids measure only weak basic sites which are not able to catalyse the hydrogen peroxide decomposition. In case of alumina-zirconia (Table 1) samples heat treated at 120°C to 800°C, and also silica-zirconia (Table 2) samples heat treated at 120°C to 500°C have strong basic sites at pK_a=9.9 and are catalytically active. A similar observation was made in case of alumina-thoria and silica-thoria. In case of silica-molybdenum trioxide, silica-tungsten trioxide, alumina-molybdenum trioxide, alumina tungsten trioxide

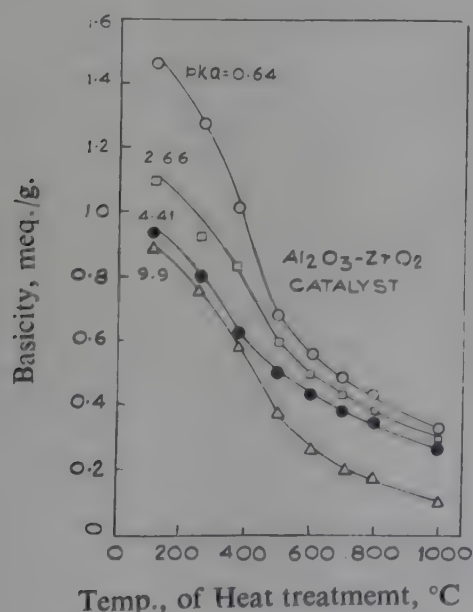


Fig. 2—Basicity vs Temperature of Heat Treatment

and also for silica-zirconia samples heat treated at 610°C and at 720°C have no basic sites at $pK_a=9.9$ but have a number of weak basic sites at $pK_a=0.64$ to 4.41 and these relatively weak basic sites are considered to be catalytically inactive. As the pK_a value of hydrogen peroxide is about 10 and it needs basic sites equal to or stronger than this for the hydrogen peroxide decomposition. This is proved by the fact that neutral red $pK_a=+6.8$ is unable to decompose hydrogen peroxide. On the basis of the observation made above, the mechanism which has been proposed earlier¹⁰ for the decomposition of hydrogen peroxide holds good in this case also.

Our observation that basic centres of $pK_a \geq 10$ are necessary for this reaction implies selectivity in the use of basic centres of particular base strength for particular reaction and a similar correlation between activity and base amount over limited ranges of base strength was evident in the decomposition of diacetone alcohol catalysed by several alkaline earth oxides¹⁵. In this case catalytic activity was found to be proportional to the basicity at $pK_a \geq +12$.

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The reaction between urea and aminoacetic acid (glycine) at pH 8 and room temperature has been found to yield a new compound, diaminoacetyl urea $(\text{NH}_2 \text{CH}_2 \text{CO})_2 (\text{NH}_4 \text{CO})$. Its unit cell parameters and space group have been determined. It belongs to monoclinic system with four molecules per unit cell having $a_0 = 8.839$, $b_0 = 12.031$, $c_0 = 5.996$ and $\beta = 94^\circ 50'$ in the space group $P2_1/n$.

Preparation and Crystallographic Data of a New Compound, Diaminoacetyl Urea

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It is well-known that urea forms complexes with many organic compounds. It was shown from this laboratory ¹⁻³ that the reaction products of urea and formaldehyde under acidic conditions were methylene diurea and dimethylene triurea. In a similar attempt to study the reaction between urea and aminoacid group the combination between urea and glycine were tried this time. Aqueous solutions of urea (Analar) and glycine (biochemical) were combined under a molar ratio 1:1 and 1:1.5, maintaining the pH of the solutions around at 8. The solutions were then refluxed on a water-bath to concentrate and were allowed to stand at room temperature for recrystallization. The crystals obtained were purified by washing successively with ethanol, mixture of water and ethanol (1:5) and finally with ether. The crystalline powders, thus obtained, were analysed by x-ray diffraction method to identify the phases formed.

The powder x-ray diffraction patterns were obtained using a 11.46 cm. diam. Guinier camera in conjunction with a crystal reflected monochromatic CuK_α radiation. For the purpose of comparison all the four samples, viz. urea, glycine and the two reaction products, were exposed in the same film.

The Guinier photograph showed that both reaction products had yielded a new compound. The reaction products I (urea : glycine 1:1) showed only a small amount of the new compound in a mixture of unreacted urea and glycine, whereas the products II

(urea : glycine 1 : 1.5) showed the formation of almost only of the new compound with very little of free urea and glycine. Then an attempt was made to identify this new compound from the data reported so far⁴. But it was found that none of the data was in agreement with the data of this compound. Therefore, an attempt was made to identify the new compound by determination of its molecular weight from single crystal lattice parameter measurements and from density.

In order to obtain single crystals the dilute aqueous solution of the product II was left for slow evaporation of water at room temperature. After a few days both needle and long hexagonal plate forms were found to crystallise out. One of the needle type crystal was used to take rotation and Weissenberg photographs along the needle axis as well as the other two mutually perpendicular directions.

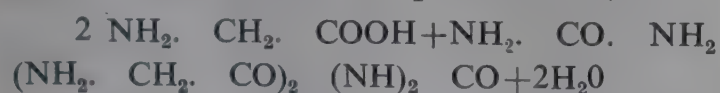
The rotation photograph along the needle axis setting showed the repeat distance to be $5.996 \text{ \AA}$. The zero-layer Weissenberg photograph of the setting gave the other two reciprocal lattice values as 0.175 and 0.128 at right angles to each other. The rotation photograph of the next setting perpendicular to the needle axis gave the repeat distance as $12.031 \text{ \AA}$. The reciprocal lattice values of this setting from zero-layer Weissenberg photograph were 0.258 and 0.175. In this setting, the angle between the reciprocal axes was found to be a non-rectangle and measured as $85^\circ 10'$. A third setting normal to both the previous settings

showed the repeat distance to be 8.839 Å. The Weissenberg photograph in this last setting gave the reciprocal lattice values as 0.128 and 0.258 at right angles to each other. From the above measurements (Table 1), it was certain that the crystal system of the new compound was monoclinic with monoclinic angle as 94° 50'. The final lattice parameter values chosen from the above measurements were: $a_0=8.839$, $b_0=12.031$ and $c_0=5.996$ Å.

TABLE 1—ROTATION AND ZERO-LAYER WEISSENBERG DATA

Needle Axis	a_0/a^*	b_0/b^*	c_0/c^*
a	8.839 Å	0.127	0.259
b	0.175	12.031 Å	0.255
c	0.175	0.125	5.996 Å

The next step was to determine the molecular weight of the compound. For this purpose a density measurement was done by displacement method in carbon tetrachloride solution. The density was found to be 1.84 g./cc. With this density value and its values of unit cell parameters determined as above the molecular weight came out to be 699 per unit cell. Out of possible reactions between urea and glycine, if the reaction had proceeded as,



the molecular weight of the resulting compound, diaminoacetyl urea would be 696 if there were four molecules per unit cell. This was practically the same as the observed molecular weight of the unit cell of the new compound. Thus, it was confirmed that diaminoacetyl urea had been formed in the reaction products studied in this paper and its density (D_x) by x-ray method was 1.83 g./c.c.

Having determined the unit cell parameters a survey was made for systematic absent reflections on the rotation and Weissenberg photographs in order to determine the space-group of the crystal system. The inspection of zero-layer Weissenberg photographs taken with crystal setting in all the three axial directions showed the following conditions limiting possible reflections:

$$\begin{array}{ll} \text{hoo} : h = 2n ; & \text{hko} : h = 2n ; \\ \text{oko} : k = 2n ; & \text{okl} : l = 2n ; \\ \text{ool} : l = 2n ; & \text{hol} : h = 2n \quad l = 2n. \end{array}$$

From the above, the condition, $\text{hko} : h = 2n$ indicate a glide plane along (001). Similarly, $\text{okl} : l = 2n$

TABLE 2—X-RAY POWDER DIFFRACTION DATA FOR DIAMINOACETYL UREA

d (Å)	I/I ₁	hkl
6.05	vw	020
4.05	s	210
3.5	vs	220
3.05	w	040
2.95	w	002,230
2.655	w	022,311
2.49	vs	31 $\bar{1}$
2.3	m	21 $\bar{2}$
2.16	w	232,410
2.125	m	042
2.03	wm	060,23 $\bar{2}$
1.9	vw	103,42 $\bar{1}$
1.88	vw	431
1.84	vw	213
1.82	vw	260
1.76	vw	252
1.75	vw	35 $\bar{1}$
1.69	vw	25 $\bar{2}$
1.67	vw	062
1.63	w	171,32 $\bar{2}$
1.61	w	17 $\bar{1}$,961
1.565	vw	43 $\bar{2}$
1.52	vw	53 $\bar{1}$
1.475	vw	172
1.465	vw	600
1.435	w	18 $\bar{1}$
1.43	vw	620
1.395	vw	27 $\bar{2}$
1.35	vw	470
1.335	vw	43 $\bar{3}$
1.3	vw	46 $\bar{2}$
1.295	vw	38 $\bar{1}$
1.275	vw	28 $\bar{2}$
1.265	vw	054,64 $\bar{1}$
1.245	vw	711
1.24	vw	254,480
1.215	vw	63 $\bar{2}$
1.195	vw	164,25 $\bar{4}$
1.175	vw	16 $\bar{4}$,264
1.15	vw	65 $\bar{1}$
1.135	vw	26 $\bar{4}$

Radiation : CuK α Guinier camera diam. 11.46cm.

reveal a glide plane along (100). The combination of these two conditions indicate a diagonal glide along (101). This diagonal glide could automatically give rise to the conditions, $h00 : h = 2n$, $00l : l = 2n$ and $hol : h = 2n ; l = 2n$. The remaining condition $oko : k = 2n$ indicate a two-fold screw axis along (010). Thus, when these symmetries were combined together in a monoclinic system the space-group turned out to be $P2_1/n$ (No. 14).

An x-ray powder diffraction pattern from pure crystals was also obtained using a Debye-Scherrer powder camera of 11.46 cm. diameter in filtered CuK_{α} radiation. The data is presented in Table 2. This is being included for the purpose of identification of this new compound by powder methods.

Thus, the reaction of urea and glycine at pH 8 and under molecular ratio 1 : 1.5 has been found to yield

a new compound, diaminoacetyl urea, which has been found to belong to the monoclinic system with unit cell parameters, $a_0 = 8.839$, $b_0 = 12.031$, and $c_0 = 5.996$ Å, with $\beta = 94^{\circ}50'$ in the space-group $P2_1/n$ (No. 14) having four molecules per unit cell.

Further work on crystal structure, optical and other properties are being attempted.

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An attempt is made to find out the origin of colour in some fluorite samples from Gujarat State with the aid of ESR studies. The colour has been found to originate due to certain defect centres in the crystals.

Electron Spin Resonance of Some Natural Fluorites

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Fluorite is very important strategic mineral of varied industrial significance. It is found in nature in various colours, viz. violet, green, yellow and blue, etc., and also as colourless crystals and opaque white lumps. Many theories have been put forward to explain the origin of colouration of fluorites but till now no conclusive explanation could be offered. The existing theories have been reviewed recently by Mackenzie and Green^{1, 2}. The one aspect where the various theories agree is that the coloration is due to some type of defect centre^{3, 4}, although the exact nature of the centre is yet to be determined. As ESR spectrometry is the best suited tool to study such centres, and as no systematic ESR data on fluorites are available, a preliminary report on some powdered samples is presented here. The samples were collected from Amba-Dongar area in Gujarat State.

Experimental

The ESR study was made on a Bruker-Physik B-ER 402 spectrometer operating at 9.5 GHz. The spectra was recorded in the first derivative mode. The samples were coloured yellow, green and violet. The colourless transparent and opaque lumps were also studied. Single crystals were ground in an agate mortar and loaded in thin-walled silica tubes. Fig. 1 shows the spectra of powdered samples. The samples were then heated up to 300°C for 4 hours to bleach out the quenchable centres. Their ESR spectra were identical to the spectrum of the white lump. Spectroscopic analysis revealed the presence of sodium, magnesium, aluminium, silicon, iron and copper. Iron and copper, the "coloured ions" were less than 10 ppm.

The impurity levels were same in all the samples. Neutron activation analysis showed the absence of rare-earth ions in the samples.

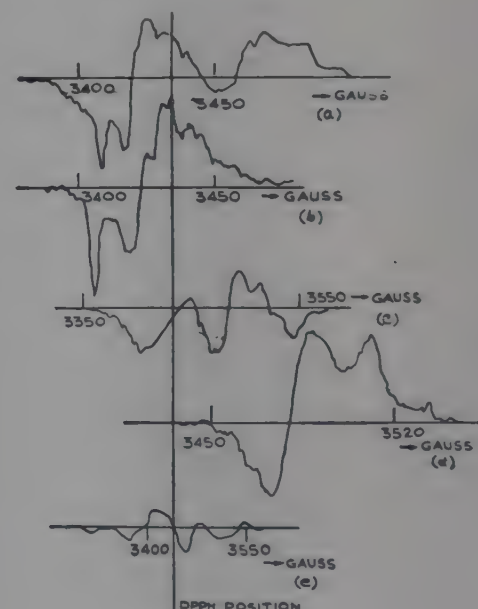


Fig. 1

(a) Colourless transparent, (b) Yellow, (c) Green, (d) Violet, (e) Opaque white lump.

Discussion

The ESR spectra is found to be shifted to higher magnetic field side as the colour changes from colourless transparent to violet. The variation in colour and the change in g-values could not be attributed to any impurities that might be present in the crystal since the impurities were identical in nature and concentration in all cases. Moreover, the transformation of these spectra to that of white lump calls for some other mechanism that may give rise to them. Colloidal calcium, whose differing particle size is postulated as a possible explanation for coloration in Blue

John⁵⁻⁷, does not explain the shift and nature of the ESR spectra with changes in colour for the fluorites under study. Therefore, some other type of defect centre must be responsible for the coloration in fluorites.

Full explanation is not possible with powder data alone and detailed ESR study of single crystals correlated with optical spectra is called for. The work has already been undertaken and will be published in due course.

Acknowledgement

We are indebted to Sri A. C. Banerjee and Dr. R. C. P. Sinha for carrying out the spectroscopic analysis and to Dr. S. K. Das and Dr. S. R. Upadhyay for neutron activation analysis of the samples. The

helpful discussion with Dr. P. K. Ghosh is also acknowledged. We are thankful to Dr. B. K. Banerjee and Sri K. C. Banerji for their kind interest in the work.

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EDITOR'S NOTE

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DTA and TGA techniques have been applied for studying the effect of different chromium compounds in the dehydration process of $\alpha - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ during calcination. The dehydration of $\alpha - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ takes place at a lower temperature ($\approx 200^\circ\text{C}$) if the duration of calcination is more than 2 hours. The dehydration process is delayed in presence of different chromium compounds. In the case of hydrated chromic (III) oxide, the elevation in the dehydration temperature is maximum.

Study of Phase Transformation of $\alpha - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in Presence Different Chromium Compounds by Differential Thermal Analysis

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Introduction

Iron oxide is an important ingredient for catalyst preparation in heterogenous mixed oxide systems. The mixed oxide, ferric oxide-chromic oxide ($\text{Fe}_2\text{O}_3 - \text{Cr}_2\text{O}_3$) is widely used for the conversion of carbon monoxide with steam at a comparatively higher temperature ($350-500^\circ\text{C}$). The mixed oxide catalysts are generally prepared by the coprecipitation method with a suitable precipitating agent. But some time mechanical mixing is also followed for commercial catalyst preparation. Bhattacharyya *et al*¹ studied elaborately the calcination process of coprecipitated gel by applying differential thermal analysis technique. Many other workers have also reported the thermal study of chromium oxide gel as well as for other chromium compounds²⁻⁵. Arora *et al*⁶ have also reported the DTA study for ferric oxide-chromium oxide mechanical mixture. In the present investigation, four different chromium compounds have been selected as a suitable source of chromium oxide and these salts have been used to investigate their effect on the dehydration process of goethite. X-ray diffraction studies on ferric oxide-chromic oxide prepared by mechanical mixing with different chromium compounds have been reported elsewhere^{7, 8}. In x-ray diffraction study, some difficulties arise due to the amorphous nature of some components present in the mixture as well as formed during calcination process. The iso-structural nature of $\alpha - \text{Fe}_2\text{O}_3$ and $\alpha - \text{Cr}_2\text{O}_3$, is also causing some problems for complete elucidation of the dehydration process. However, these difficulties have been overcome with DTA and DTGA studies.

Experimental

Preparation of Samples : The iron oxide mass was prepared by reacting ferrous sulphate solution (II) with ammonium carbonate (IM) solution. The precipitated mass was thoroughly washed and oven-dried ($110 \pm 5^\circ\text{C}$) for 6 hr and then mechanically mixed thoroughly with the requisite amount of different chromium compounds (to give about 15 per cent chromic (III) oxide to the finished samples). The respective pastes were oven-dried at $110 \pm 10^\circ\text{C}$ for 6 hr. The samples were designated as A_1 , A_2 , A_3 and A_4 according to the chromium compounds used i.e. chromium (VI) oxide, ammonium dichromate, chromium acetate and hydrated chromic (III) oxide respectively and the parent iron oxide mass was designated as A.

Differential Thermal Analysis : DTA of the samples A_1 , A_2 , A_3 and A_4 as well as the parent iron oxide mass was carried out in a fully automatic model Linseis instrument in the temperature range $30-600^\circ\text{C}$. The measuring head used was made of nickel block and the thermo-couples were chromel-alumel. The rate of heating was controlled at about $10^\circ\text{C}/\text{min}$. by a programme controller and $\alpha - \text{Al}_2\text{O}_3$ was used as reference material. The thermograms are shown in Fig. 1 and the peak temperatures are given in Table 1.

Derivative Thermogravimetric Analysis (DTGA)
Thermogravimetric analysis of all the samples was carried out in an apparatus fabricated in this laboratory, in the temperature range $30-600^\circ\text{C}$. The rate of heating was controlled at about $10^\circ\text{C}/\text{min}$.

TABLE 1—DTA AND DTGA THERMOGRAM PEAK TEMPERATURES OF FIVE DIFFERENT SAMPLES

Samples	DTA Peak Temperatures, °C		DTGA Peak Temperatures, °C
	Exo	Endo	
1. Iron oxide mass (A)	—	140 s 320 s	40-150 s 285-320 m
2. A ₁ Iron oxide mass + chromium (VI) oxide	—	120 s 190 m 240 s 330 s 410 m	40-140 s 170-210 m 330-350 m 390-420 m
3. A ₂ Iron oxide mass + ammonium dichromate	410 m	125 s 210 s 380 s	40-130 s 200-210 s 370-385 m
4. A ₃ Iron oxide mass + chromium acetate	420 m	120 s 320 s 375 m	40-130 s 250-325 s 375-390 m
5. A ₄ Iron oxide mass + hydrated chromic (III) oxide	410 m	135 s 275 s 390 m	110-140 s 240-310 s 380-390 m

*s — strong, m — medium

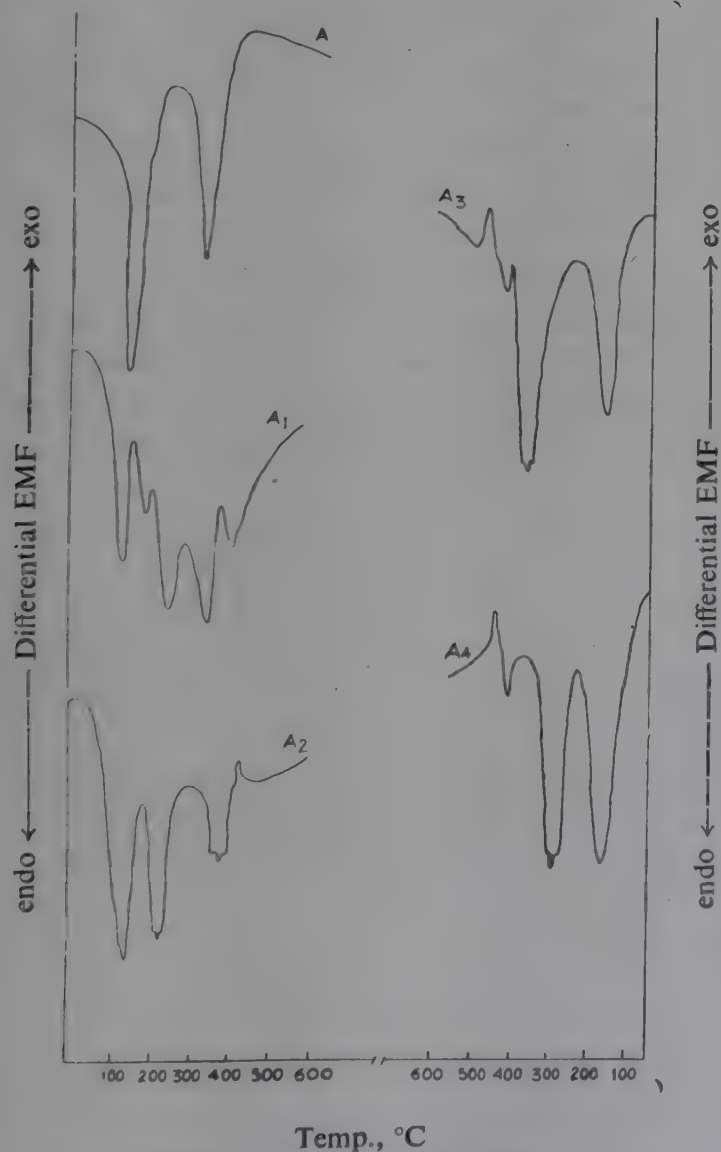


Fig. 1—DTA Thermograms of Samples A, A₁, A₂, A₃ and A₄

a variable voltage regulator. The plot of dw/dt against T are shown in the Fig. 2 and the decomposition ranges are given on the Table 1. The chemical analysis and crystal phase composition of A, A₁, A₂, A₃ and A₄ are given in Table 2. The crystalline phase was determined by x-ray diffraction technique using FeK_{α} radiation as described elsewhere⁸.

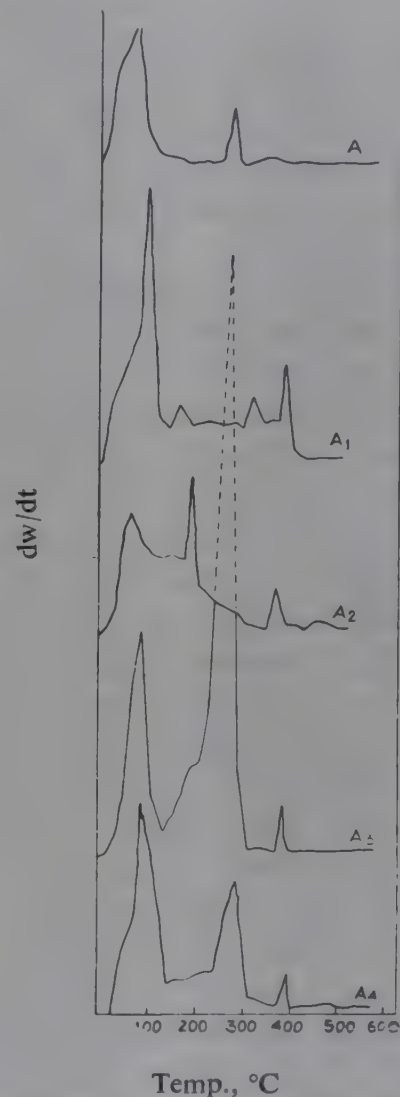


Fig. 2—DTGA Thermograms of Samples A, A₁, A₂, A₃ and A₄

Results and Discussion

Sample A: The derivatogram of hydrated iron oxide mass is shown in Fig. 1. The DTA curve shows two endothermic peaks at 140 and 320°C; the peak at 140°C is due to the absorbed moisture and loosely bound water molecules, whereas second peak is encountered due to the phase transformation of goethite into $\alpha-Fe_2O_3$ ^{9, 10}. DTGA curves give a similar picture regarding the dehydration of goethite with the increase in temperature. The first weight-loss was encountered in the range 40-150°C and another peak at 285-320°C.

Sample A₁: The incorporation of chromic (VI) oxide in iron oxide mass showed five endothermic

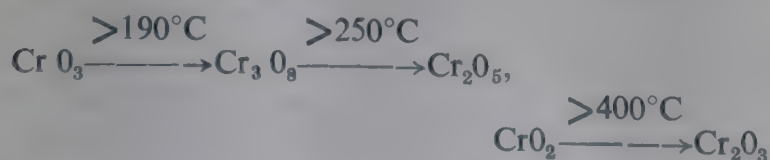
TABLE 2—CHEMICAL ANALYSIS AND CRYSTAL-PHASE COMPOSITION OF THE FIVE SAMPLES

Samples	L.O.I. at 900°C, %	Fe ₂ O ₃ , %	Cr ₂ O ₃ , %	Crystal Phase	
				Oven-dried* at 110 ± 5°C	Cured at 400°C ± 10°C** for 4 hr
1. A	12.41	87.71	—	α-Fe ₂ O ₃ ·H ₂ O γ-Fe ₂ O ₃ (trace)	α-Fe ₂ O ₃
2. A ₁	11.65	74.21	14.45	α-Fe ₂ O ₃ ·H ₂ O γ-Fe ₂ O ₃ (trace)	α-Fe ₂ O ₃
3. A ₂	10.88	74.42	14.81	α-Fe ₂ O ₃ ·H ₂ O γ-Fe ₂ O ₃ (trace) (NH ₄) ₂ Cr ₂ O ₇	α-Fe ₂ O ₃
4. A ₃	11.20	74.13	14.64	α-Fe ₂ O ₃ ·H ₂ O γ-Fe ₂ O ₃ (trace)	γ-Fe ₂ O ₃ α-Fe ₂ O ₃
5. A ₄	12.85	73.54	13.82	α-Fe ₂ O ₃ ·H ₂ O γ-Fe ₂ O ₃ (trace)	α-Fe ₂ O ₃

*In case oven dried samples chromium salts is not detectable in x-ray diffraction pattern, except (NH₄)₂Cr₂O₇, due to their poor crystalline character.

**In cured samples, Cr₂O₃ is not detectable in x-ray diffraction pattern.

peaks at 120, 190, 240, 330 and 410°C. The first endothermic peak at 120°C was due to the loss of absorbed moisture while the second peak at 190°C was due to the dehydration and decomposition of CrO₃ into other intermediate oxides. This peak was followed by another endothermic peak at 240°C which was probably due the formation of another intermediate oxide of chromium having lower oxidation number. The endothermic peak at about 330°C was due to phase transformation of goethite into α-Fe₂O₃, as well as formation of lower valency chromium oxides. These intermediate oxides of chromium finally get converted into chromic (III) oxide around 410°C, which is indicated by another endothermic peak. The intermediate endothermic peaks have been assigned from the nature of thermal decomposition of chromium (VI) oxide as revealed from x-ray diffraction study on the calcination process of chromium (VI) oxide in air^{7, 11}. The course of decomposition is represented as



The first weight-loss, encountered in DTGA curve in the range 40-140°C, was solely due to the loss of absorbed moisture and loosely bound water. The second weight-loss, encountered in the range 170-210°C, was due to the decomposition and dehydration of chromic acid. α-Fe₂O₃·H₂O dehydrates in the range 330-350°C, as well as causes the formation of intermediate oxides of chromium which finally converted into chromic (III) oxide in the range 390-420°C. These results are also supported by DTA results.

Sample A₂: In case of sample, A₂, three endothermic peaks were noticed in DTA curve, at 125, 210 and 380°C the first one due to the absorbed moisture, the second being the decomposition temperature of ammonium dichromate into chromic (III) oxide and the last one was, where goethite converted into α-Fe₂O₃. Another exothermic peak at 410°C was due to crystallization of amorphous chromic oxide into crystalline α-Cr₂O₃. J. Burzyk *et al*⁵ noticed two exothermic peaks having their maximum at about 280 and 430°C, in case of pure ammonium dichromate. The last exothermic peak at 410°C was due to the crystallization of chromic (III) oxide from its amorphous state. But the first exothermic peak was not noticed probably due to the low concentration of ammonium dichromate dispersed in iron oxide matrix. The DTA results are also fully supported by DTGA curves. The first weight-loss was encountered at 40-130°C due to the absorbed moisture and the second weight-loss at 200-210°C, which is the decomposition temperature of ammonium dichromate. Further weight-loss encountered around 370-385°C is assigned to be due to the conversion of goethite into α-Fe₂O₃.

Sample A₃: In case of sample A₃, DTA curve showed second endothermic peak at 320°C, where chromium acetate decomposes into chromium (III) oxide with a minor amount of other intermediate oxide. The other endothermic peak at 375°C is assigned for the dehydration of goethite into α-Fe₂O₃. The last exothermic peak at 420°C was due to the conversion of γ-Fe₂O₃ into α-Fe₂O₃, as x-ray diffraction study indicated that the formation of γ-Fe₂O₃, phase is pronounced by the use of acetate salt with goethite.

The second weight-loss in DTGA curve was due to the decomposition of chromium acetate which is similar to the DTA peak around 325°C. The weight-loss observed at 375-390°C was due to the dehydration of goethite into α -Fe₂O₃.

Sample A₄: The sample A₄ showed first endothermic peak in DTA curve at 135°C which is due to the absorbed moisture and loosely bound water in chromium oxide gel as well as with iron oxide mass. The second endothermic peak at 275°C was due to the loss of the rigidly bound water with hydrated chromic oxide gel and the other endothermic peak at 275°C was due to the loss of the rigidly bound water with hydrated chromic oxide gel and the other endothermic peak at 390°C due to the dehydration of goethite into α -Fe₂O₃. The last exothermic peak at 410°C was is due to the conversion of amorphous chromium (III) oxide into crystalline chromic oxide^{1, 3}.

The first weight-loss, encountered in DTGA curve at 110-140°C, was due to the absorbed moisture and loosely bound water molecule with hydrated chromic oxide gel as well as with iron oxide mass. The second peak in DTGA curve at 240-310°C was assigned due to the dehydration of rigidly bound water molecule with chromic (III) oxide gel. The weight-loss at 380-390°C was assigned to the conversion of goethite into α -Fe₂O₃.

As revealed from the DTA and DTGA studies, the dehydration of goethite was affected in the presence of different chromium compounds due to their different mode of thermal decomposition. Another interesting fact emerging from this study is that the dehydration takes place at a lower temperature if the duration of calcination was more⁸. The dehydration process was delayed in presence of different chromium compounds as is evident from DTA and DTGA curves (Figs. 1 & 2). The dehydration peak for goethite shifted in the case of different samples from 320 to 380°C incase of sample A₂, 320 to 375°C in the case of A₃ and 320 to 390°C in the case of A₄. Incidentally, it can be noted that the present findings are not in full agreement with those of other workers⁶ in the case of sample A₁ where CrO₃ has been used for impregnation. The formation of chromic oxide from CrO₃ requires a higher temperature than 400°C; before attaining this temperature, goethite transform into α -Fe₂O₃ during the course of calcination as observed in the previous studies^{7, 8}. Hence, the iso-structural influence of α -Cr₂O₃ to the goethite dehydration process is not clearly understood⁶. Further in

the present investigation some other endothermic peaks appeared in the DTA and DTGA curves (Fig. 1 & 2) which was not reported by earlier workers. The additional peaks are well expected as the formation of Cr₂O₃ takes place through different intermediate oxides of chromium¹¹.

The attainment of dehydration temperature of goethite was much delayed in the cases of samples A₂, A₃ and A₄ as compared to that of A₁. In case of sample A₁, chromic (III) oxide was formed around 400°C, though some other intermediate oxides of chromium were present in the earlier stage of calcination, whereas in case of sample A₂, A₃ and A₄, α -Cr₂O₃ was formed at the temperature region which is much below the dehydration temperature of goethite. This elevation in dehydration temperature of goethite was due to the iso-structural nature of α -Fe₂O₃ with α -Cr₂O₃. In the cases of hydrated chromic (III) oxide gel, the elevation was maximum.

Acknowledgements

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Molybdenum (V) complex of 5,5'-thiodisalicylic acid has been prepared. The octahedral stereochemistry is postulated for this complex on the basis of chemical analysis, magnetic susceptibility, infrared, ultraviolet and visible spectral data. The thermodynamic stability constants of the complex have been determined in solution and the results indicate the formation of 5:8 :: metal : ligand complex.

Molybdenum (V) Complex with 5,5'-Thiodisalicylic Acid

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The complexes of molybdenum have been a subject of extensive investigation because molybdenum is involved in the catalysis of several oxidation-reduction reactions in biochemical system. It is known to form a coloured complex with 5,5'-thiodisalicylic acid¹ (hereafter abbreviated as TDSA). Recently, more quantitative studies have been reported in literature²⁻⁸ regarding the complexation reactions of TDSA. The present investigation was undertaken with a view to obtaining some quantitative data regarding the complexes of molybdenum -(V) with TDSA. The complex has been isolated and characterized by the elemental analysis and magnetic susceptibility measurements and its mode of coordination has been discussed in the light of i.r. spectra. The complex formation has also been studied potentiometrically. The method of Bjerrum¹⁴, as modified by Irving and Rossotti¹⁵ and Rossotti and Rossotti¹⁶, has been used for calculating stability constants from potentiometric data.

Experimental

TDSA sample* was of 99.7 per cent purity and fresh solutions of the substance were prepared in absolute alcohol whenever needed. A stock solution of ammonium molybdate was prepared from an Analar grade reagent. All other reagents used were also of Analar grade.

The magnetic susceptibility measurements were made by Gouy's method using mercury (II) tetrathio-cyanato cobaltate (II) as the calibrating reagent at 30°C.

The infrared spectra of the TDSA and its complexes were recorded on a Perkin-Elmer (model-521) recording spectrophotometer in the range of 4000 to 250 cm⁻¹.

The absorption spectra of the complex were recorded with Cary 14 spectrophotometer provided with an automatic recording system. The spectra were taken in nujol mull.

The analysis of the metal and sulphur in the complex was carried out by the standard method¹³. Carbon and hydrogen analyses were carried out at the Micro-analytical Section of the Indian Institute of Technology, Kanpur.

A Leeds-Northrup pH-meter fitted with a general purpose glass electrode was used for potentiometric titrations and other pH measurements. The medium of titration was kept 60 per cent alcoholic. Perchloric acid and sodium perchlorate were added to maintain constant ionic strength. The solvent, the ligand and mixture of metal and ligand were titrated against the standardized 0.1M sodium hydroxide (60 per cent alcoholic) solution. The following solutions were titrated separately keeping the total volume 50 ml.

- (i) 5 ml. 0.01M HClO₄ + 5 ml. 0.01M Na ClO₄ + 30 ml. ethano + 10 ml. water
- (ii) 5 ml. 0.01M HClO₄ + 5 ml. 0.01M NaClO₄ + 25 ml. 0.01M TDSA + 5 ml. ethanol + 10 ml. water.
- (iii) 5 ml. 0.01M HClO₄ + 5 ml. 0.01M NaClO₄ + 25 ml. 0.01M TDSA + 5 ml. ethanol + ml. 0.01M molybdenum solution + 5 ml. water.

* From Eastman Organic Chemicals.

Preparation of Complex: 50 ml. of 0.1M ammonium molybdate solution was added to 200 ml. of 0.1M TDSA ethanolic solution, pH of the resulting solution being 4.0. The solution mixture was concentrated on a water-bath and a red precipitate was obtained, which was dissolved in water and concentrated again. This process was repeated. The complex was dried at 80°C, the yield being 1.0 g. The complex was soluble in water and alcohol giving red coloured solution. It melted at 235°C. The analysis of the complex for metal, sulphur, carbon and hydrogen showed 2 : 3 :: metal : ligand stoichiometry. $H_2[Mo_2O_3(C_{14}H_8O_6S)_3 \cdot 2H_2O]$ required Mo = 16.18 per cent, S = 8.07 per cent, C = 42.35 per cent and H = 2.69 per cent and has been found to contain Mo = 16.25 per cent, S = 8.20 per cent, C = 43.00 per cent and H = 2.73 per cent.

Molar conductance of the complex in aqueous solution comes out to be 330 mhos, suggesting the compound to be univalent electrolyte. Anionic nature of the complex is further revealed by migration of coloured ions toward anode. The molecular weight of the complex has been determined by the cryoscopic method and comes out to be 450.

Results and Discussion

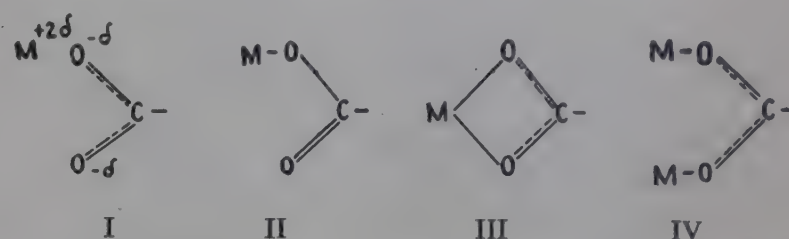
Molybdenum (V) has the electronic configuration $4d^1$. Mo (V) complexes should, therefore, exhibit the magnetic moment value for one unpaired spin. The complex in question showed magnetic moment value of 1.37 BM. The detailed experimental results are given in Table 1. The complexes of Mo (V) showed greater tendency to polymerize⁹. The ligand TDSA forms complexes of polymeric nature⁵⁻⁷. The lowering of the magnetic moment value may be due to the metal-metal interaction in the complex. The electronic spectra of the complex did not show any definite band, which can throw some light on its stereochemistry. A very weak band at 14,900 cm^{-1} arose which may be due to crystal field band¹⁰.

Table 1—Magnetic Measurement Data

Complex	$X_g \times 10^6$, c.g.s.	$X_M \times 10^6$, c.g.s.	$X_{M(corr)} \times 10^6$, c.g.s.	μ_{eff}
$H_2Mo_2O_3(TDSA)_3$	1.01	1201.90	1574.1	1.37
$2H_2O$	1.31	1201.90	1574.1	1.37

The infrared spectra of the ligand and complex were examined to establish the structure of the complex. The i.r. spectrum of TDSA showed bands at

1660, 1600, 1200 and 3360 cm^{-1} which may be assigned to $\nu_{asym} C \leq^0 \nu_{sym} C \leq^0$, $\delta C \leq^0 + \nu C-O$ and $-HO$ stretching vibrations. Comparing this with i.r. spectrum of the complex, it was found that the band corresponding $\nu_{asym} C \leq^0$ and $\delta C \leq^0 + \nu C-O$ frequencies shift towards the lower position in the complex indicating coordination through C-O group of carboxylic acid and suggest unidentate coordination of these groups. In Table 2 are listed such bands appearing in complex studied here. Out of the following four possible modes¹¹ of coordination of carboxylic group the data clearly favour the structure II for the complex in question.



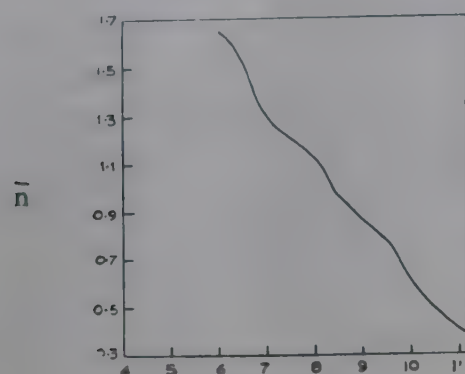
The bands appearing at 3360 cm^{-1} lies in the range of OH stretching vibration but its broad nature and intense intensity as compared to the free OH vibration suggests that it may be due to intramolecular hydrogen bonding. The spectra of complex show a new band at 400 cm^{-1} may be assigned to M-O band¹². The two chelating sites in the ligand molecule perhaps coordinate giving rise to a polymerisation⁴⁻⁶.

Table 2—Infrared Spectral Data

Compound	$\nu_{asym} C \leq^0$ cm^{-1}	$\nu_{sym} C \leq^0$ cm^{-1}	$\delta C \leq^0$ cm^{-1}	$+ \nu C-O$	$\nu M-O$ cm^{-1}
TDSA	1660	1600	1200	—	—
$H_2Mo_2O_3(TDSA)_3$ $2H_2O$	1545	1600	1150	—	400

Potentiometric Studies: The respective metal ions with the ligand were titrated against alkali. A displacement was noticed in metal titration curve with ligand titration curve indicating liberation of proton due to complex formation. The plots of pH vs volume of alkali added gave S shaped curves. From the titration curves of the solutions (I) and (II), the $\bar{n}_H$ values were calculated at different pH. From the shift of the titration curves of solution (II) and (III) the stoichiometry of the complex was found to be 5 : 8 :: metal : ligand. The average number of ligands ($\bar{n}$) attached per metal ion and free ligand exponent (pL) were calculated at the same pH value at which $\bar{n}_H$ values were calculated². The $\bar{n}$ values were plotted against pL values (Fig. 1). The values

of pL at $\bar{n}=0.5$ and 1.5 gave stepwise stability constant $\log K_1$ and $\log K_2$ respectively. The values of stepwise stability constants $\log K_1$ and $\log K_2$ were found to be 10.50 and 6.55 respectively.



PL
Fig. 1

Acknowledgements

The author is thankful to Dr. H. L. Nigam, Department of Chemistry University of Allahabad, and Dr. B. K. Banerjee, Superintendent Physical Research Wing of Planning & Development Division, FCI Ltd., for their keen interest in this work and for valuable discussions.

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[Original mass. received on Jan. 18, 1974]

In the present study it has been shown that granular TSP can be blended with calcium ammonium nitrate (CAN) without much loss of water-soluble P_2O_5 . The effect of free phosphoric acid in TSP caused an initial rapid reversion of the water-soluble component. The reversion is found to increase with the increase in the moisture content of TSP and decrease in the granular size of components of the blend.

Granular Blends of Triple Superphosphate and Calcium Ammonium Nitrate

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Blending of fertilizers is of considerable significance for the balanced nutrition of the crops. In our previous studies^{1,2}, the extent of reversion of water-soluble P_2O_5 to water insoluble form was determined at various intervals of time with superphosphate (17 per cent water-soluble P_2O_5) blended with CAN containing 25 per cent nitrogen to give a product having a nutrient ratio 2-1-0. Similar particle size distribution of both the components were maintained to prevent segregation of constituents. In the present work, similar studies are reported with triple superphosphate (TSP) and CAN blended in a proportion to give 1-1-0. It is commonly believed that CAN and superphosphates are incompatible due to the reversion of the water-soluble P_2O_5 to water-insoluble form as monocalcium phosphate (MCP) reacts with calcium carbonate of limestone to form dicalcium phosphate dihydrate which is water-insoluble.

Experimental

The powdered TSP (total P_2O_5 48.33 per cent, water-soluble P_2O_5 47.24 per cent and citrate-soluble P_2O_5 0.28 per cent) was granulated in a paddle type granulator. Good granules were obtained when a large portion of water was initially added and the slurry was processed at a temperature of 70-100°C to obtain a pasty mass for granulation.

CAN used in this study was obtained from the Nangal Unit of FCI. In two of the samples, H_3PO_4 was added at the time of preparation of granular TSP

to study the effect of free phosphoric acid on the extent of reversion of water-soluble P_2O_5 . Granular TSP and CAN before mixing were dried to a constant weight over concentrated sulphuric acid then the required amount of moisture was introduced by exposing the samples to 100 per cent relative humidity. These samples were kept for a day so that the moisture gets evenly distributed. Then the two components were blended in the ratio 1-1-0, and placed in air-tight bottles at the room temperature ($\sim 30^\circ\text{C}$). 0.5 g. of samples were withdrawn and analysed for water-soluble and citrate-insoluble phosphates. The nitrogen content of CAN was 25 per cent.

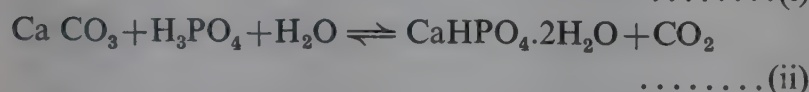
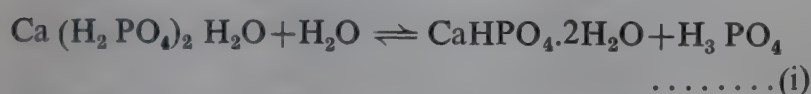
Results & Discussion

The results obtained so far show that size of granule and amount of moisture present in the sample influenced the extent of reversion of phosphate from water-soluble to water-insoluble form. They further reveal that the reversion of water-soluble P_2O_5 is not very significant even after storage for a period of 1-2 months and TSP in granular form can be considered compatible with CAN. The reversion is expected to be more pronounced when powdered TSP is used. This is understandable as the area of contact between constituents increases significantly when powdered TSP is used resulting in increased reaction between TSP and calcium carbonate causing an increase in the extent of reversion of monocalcium phosphate (MCP) to water-insoluble dicalcium phosphate dihydrate.

TABLE 1—PERCENT REVERSION OF WATER-SOLUBLE PHOSPHATE IN 1-1-0 BLEND CONTAINING GRANULAR CAN AND TSP

Moisture contents of the Blend			Time, Days							
TSP	CAN		1	15	30	60	90	120	150	180
A	(-5+6) 4%	(-5+6) 2%	1.94	17.62	27.44	34.63	46.35	49.00	50.31	53.54
B	(-6+8) 4%	(-5+6) 2%	2.60	15.03	28.03	37.89	43.12	49.00	50.97	54.22
C	(-8+10) 4%	(-5+6) 2%	1.94	15.66	30.13	38.55	47.24	50.97	51.63	54.89
D	(-10+16) 4%	(+5,20-25) 2%	1.94	18.94	20.25	28.03	35.95	48.38	53.54	58.19
E	(-5+8) 4%	(-5+6) 2%	4.16	13.09	15.47	28.57	39.88	45.83	49.40	52.40
F	(+5) 4%	(-5+6) 2%	0.63	14.37	17.62	32.01	37.89	41.17	47.72	52.90
G	(+5) 4%	(+5) 2%	1.29	13.72	21.57	23.03	34.63	43.73	48.35	49.00
H	(-5+6) 4%	(-5+6) 1%	1.29	18.24	26.25	34.63	39.87	45.75	49.00	54.89
J	(-5+6) 8%	(-5+6) 2%	2.60	24.83	30.06	37.23	44.43	53.64	56.19	59.03

The extent of reversion of the P_2O_5 is dependent on the dissolution and hydrolysis of MCP in water and the phosphoric acid then reacts with calcium carbonate. When free phosphoric acid is present reversion rate is initially fast as shown in the table. After the free phosphoric acid is neutralized, the extent of reversion depends on the dissolution and hydrolysis of MCP⁵ that continues at slow rate.



Phosphoric acid formed as a result of the hydrolysis of MCP is neutralized by calcium carbonate according to the reaction (ii) and the removal of H_3PO_4 from the system shifts the equilibrium of reaction (i) to right and monocalcium phosphate is converted to dicalcium phosphate dihydrate.

About 50 per cent reversion occurs within a period of 180 days. When the particle size of the compo-

nents of the blends is relatively small (samples C & D) the extent of reversion is enhanced. This is so because the increased area of contact per unit weight of the blend in case of the smaller granules. With sample containing 5% phosphoric acid reversion is relatively fast due to the almost instantaneous neutralization of free acid by lime stone. The extent of reversion is also dependent on the amount of moisture in TSP. This is clearly evident from the results of sample J containing 8 per cent moisture.

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The reaction of sodium borohydride in iso-propyl alcohol with chalkone (phenyl styryl ketone) shows simple second order kinetics; first order in the concentration of borohydride and first order in the carbonyl component. Chalkone reacts faster than acetone and acetophenone with the borohydride. On this basis, a mechanism has been suggested. The energy of activation for the reaction was found to be 23.00 Kcal./mole.

Kinetics of the Reduction of Chalkone With Sodium Borohydride

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A number of reactions have been studied to examine the effect of structure on the reactivity of aldehydes and ketones with reagents such as hydroxylamine¹, phenyl hydrazine², and semi-carbazide³. The discovery of sodium borohydride⁴ made available a convenient reagent which rapidly reduces carbonyl compounds in suitable solvents⁵. It was demonstrated by Garrett and Lyttle⁶ that the reduction of 3 α -hydroxy-11 α -acetoxy-pregnan-20-one by sodium borohydride was second order. Relatively rough kinetic studies have indicated that this reaction holds promise for the investigation of structural effects⁷⁻⁸.

In the present investigation, the study of kinetics of the reaction of sodium borohydride with chalkone (α , β -unsaturated ketone) was undertaken in order to find out the effect of the double bond upon the reduction of the carbonyl group by borohydride.

Isopropyl alcohol was selected here as the reaction medium as it exhibits no measurable reaction with borohydride over extended period of time⁹.

Experimental

Reagents: Iso-propyl alcohol was dried by standing over sodium borohydride for 24 hr and then heated under reflux for 2 hr. It was fractionally distilled and had boiling point 81-82°C at 750 mm. laboratory grade (B.D.H.) sodium borohydride was taken and the chalkone (phenyl-steryl ketone) was

prepared and purified according to the method of Rout *et al*⁹.

Rate Measurement: Standard solutions of sodium borohydride and of carbonyl component in iso-propyl alcohol were prepared. A known volume of the sodium borohydride solution was placed in a reaction flask with a long narrow neck, immersed in the constant temperature bath. A known volume of the chalkone solution, at reaction temperature, was added to the borohydride solution with vigorous mixing. At intervals, 10 ml. portions of the reaction mixture were withdrawn, added to a mixture of 1 ml. (N) sodium hydroxide and 25 ml 0.1 (N) potassium iodate. After standing for 3-5 min. 2 g. of potassium iodide was added, followed by 2.5 (N) sulphuric acid and 200 ml. of water. The liberated iodine was titrated with standard sodium thiosulphate using starch as indicator.

Under these conditions of excess of borohydride, the reaction was first order in ketone alone. The first order rate coefficients were determined by the expression,

$$k_1 = 1/t \ln (a/a - 4x) \quad \dots\dots\dots (1)$$

where 'a' is the initial ketone concentration and (a-4x) is the concentration of ketone at 't' time. The second order rate coefficient 'k' was then calculated from the known standard borohydride concentration 'b' as:

$$k = k_1/4b \quad \dots\dots\dots (2)$$

The rate constants at 40, 45 and 50°C together with the energy of activation are given in Table 1.

Table 1—Rate Constants and Engineers of Activation

Tempe- rature, °C	Concen- tration of Chal- kone, N	Concentra- tion of Sodium Borohy- dride, N	$k \times 10^{-3}$ lit. mol. ⁻¹ sec. ⁻¹ , °C	E _{act} , Kcal./mole
40	0.005	0.05	4.40	—
45	0.005	0.05	10.87	23.00
50	0.005	0.05	17.75	—

Mechanism of the Reaction: The mechanism and rates of reaction of a number of ketones and aldehydes with sodium borohydride in isopropyl alcohol have been investigated by Brown *et al*¹⁰⁻¹³. The reaction was considered to proceed with a rate-determining transfer of the first hydrogen atom of the borohydride ion to the carbonyl carbon. From their study of the rate of sodium borohydride reaction of acetone and acetophenone, they reported that acetophenone reacts at a slower rate than acetone which supports the above mechanism. The resonance interaction of the phenyl group with the carbonyl group increases the electron density on the carbonyl group and diminishes its reactivity towards borohydride. In case of chalkone ($C_6H_5-CO-CH=CH-C_6H_5$) there is one double bond between the $>C=O$ and the phenyl group. So, according to the mechanism given by Brown *et al*, the rate of the reduction of the chalkone should be considerably reduced than acetophenone. But the result is surprising. Chalkone reacts faster than acetone. This fact suggests that the above mechanism probably does not hold good in the case of chalkone.

Jackson *et al*¹⁴ in their study of the borohydride reduction of α , β -unsaturated ketone suggested a 1, 4-addition mechanism. With this mechanism the greater reactivity of chalkone than acetone can be best

explained. Thus, the 1,4-addition mechanism has been supported for the borohydride reduction of chalkone.

Acknowledgements

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Application of wheat straw and urea as nitrogen source to submerged soil conditions revealed a beneficial effect of combined application of straw nitrogen and urea nitrogen upto 2 months with respect to nitrogen mineralized or lost from ^{15}N tagged wheat straw. An increase of straw-nitrogen in soil organic-nitrogen pool was noticed in 4 months with this treatment, which may be beneficial for maintaining the fertility for the succeeding wheat crop.

Transformation of Applied Nitrogen as Wheat Straw and Urea under Submerged Soil Conditions—Studies with ^{15}N

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Growing rice after wheat is becoming an extensive practice in Northern India, particularly in Punjab and Haryana. With introduction of high-yielding varieties and mechanization of farm operations, a large amount of straw is now available for being buried in the soil and thus the knowledge about the nitrogen transformation of added wheat straw is important. The present investigation has been carried out using ^{15}N as a tracer to obtain precise information on the nature of nitrogen release from the straw and fertilizer under the submerged soil conditions.

Experimental

The experiment consisted of an incubation study with a sandy loam alluvial soil under submerged soil conditions (4 to 5 cm. standing water), brought from the Indian Agricultural Research Institute's farm at New Delhi, where wheat-rice rotation was followed for the last 5 years. The pH of the soil was 8.1, and its carbon,¹ clay and total nitrogen contents were 0.56, 28 and 0.067 per cent, respectively. The treatments were as follows: (a) ^{15}N -tagged wheat straw (0.6 per cent nitrogen) at 100 kg. N/ha; (b) ^{15}N -tagged urea at 100 kg. of N/ha; and (c) ^{15}N -tagged wheat straw + untagged urea; each at 50 kg. of N/ha.

The straw had 0.535 atom per cent excess of ^{15}N while the urea was labelled with 1.000 atom per cent ^{15}N .

A basal dose of phosphorus at 80 kg P_2O_5 /ha as superphosphate and potash @ 60 kg K_2O /ha as muri-

ate of potash was also applied. The study was carried out in 5 kg. capacity plastic pots having no hole as for drainage. In all, there were 3 treatments and 2 replications for each time of sampling, viz. at 2 and 4 months interval.

The soil samples collected for both time of interval were analysed for total carbon and nitrogen and for ^{15}N atom per cent excess in the mineralizable nitrogen fraction of the soil as well as the total ^{15}N content².

Results and Discussion

A balance sheet of the applied nitrogen is presented in Table 1 along with the C/N ratio at both 2 and 4 months interval. The results revealed that the total mineralization rate of the applied nitrogen as urea under the experimental conditions was maximum at both the stages of sampling and also increased with time. The mineralization of straw-nitrogen also increased with time but to a smaller extent. On the contrary, the combined application of urea and wheat straw in equivalent amounts of nitrogen (50 kg. N/ha each) showed a considerable reduction in mineralizable nitrogen from the straw, with time.³

The decomposition of straw was slow upto 2 months and consequently a major portion of the straw-nitrogen remained in the organic form (74 per cent). In the combined treatment (c) the decomposition of straw was enhanced due to the presence of urea and thus only about 58 per cent of the straw-

nitrogen was in organic fraction. The application of urea nitrogen alone showed only about 50 per cent in the organic form. At 4 months sampling time an appreciable amount of straw might have been decomposed and thus only about 32 per cent of the straw-nitrogen was in the organic form; the combined treatment (c) also showed the same trend but the decomposition was slow in this case. The urea-nitrogen also got reduced in the organic fraction, may be the remineralization of the urea-nitrogen have been started (an increase in mineralizable urea-nitrogen is clear from the Table 1).

TABLE 1—TRANSFORMATION OF NITROGEN APPLIED IN THE FORMS OF WHEAT STRAW AND UREA UNDER SUBMERGED SOIL CONDITIONS

(Incubation Studies)

nitrogen level 4.56 mg./100g. soil

Treatment	% Mineralization of the Applied N	% of the Applied N in Organic Form	Loss from the Applied Nitrogen, %	NH ₄ /NO ₃ Ratio in the Mineralizable N	C/N Ratio
2 Months' Sampling					
(a) Straw*	20.75	74.29	4.96	2.6	8.4
(b) Urea*	31.80	50.18	18.02	1.8	7.4
(c) Straw* + Urea	26.22	57.58	16.22	6.6	8.0
4 Months' Sampling					
(a) Straw*	34.55	31.75	33.20	1.2	7.4
(b) Urea*	31.80	24.64	34.23	0.6	5.8
(c) Straw* + Urea	18.62	45.28	36.10	0.8	6.4

*Asterisk denotes ¹⁵N tagged fertilizers.

The losses of applied nitrogen when studied showed a considerable variation in the values. At first stage

of sampling it was maximum where urea-nitrogen was applied and was minimum where straw-nitrogen was applied. At 4 months' time the losses tended to become more or less equal with slightly high from straw where it was applied along with urea. The maximum of straw-nitrogen (when applied along with urea) in organic fraction and also the maximum loss of nitrogen from this source at 4 months' period may be attributed the cause of low mineralizable-nitrogen fraction at this sampling time.

The above findings show that mixing wheat straw and urea is beneficial upto 2 months, as it releases appreciably high amounts of mineralizable nitrogen from the straw which could be efficiently utilized by the succeeding crop (rice) upto this period. At 4 months sampling time the mineralization get reduced and a higher amount of straw-nitrogen was seen in the organic fraction which may ultimately enrich soil in total nitrogen. This may also help in build up of organic matter which may be useful for the succeeding wheat crop with respect to soil structure which usually deteriorates due to puddling for paddy.

Acknowledgement

The authors are thankful to Mass Spectrometric Unit of Nuclear Research Laboratory, for the ¹⁵N assay.

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[Original mss. received on Jan. 19, 1974]

Polarographic studies have been carried out on a nickel-55' thiodisalicic acid system with a dropping mercury electrode. The stoichiometry of the complex has been found to be 1:1 (metal:ligand) in acetate buffer (pH 4.8). The complex is reduced irreversibly at the d.m.e. with a transfer coefficient (α) 0.348. The forward rate constant K^0_f for the electrode reaction as calculated from Matsuda and Ayabe's equation has been found to be $4.02 \pm 0.05 \times 10^{-17}$.

Studies on Irreversible Electrode Process : A Note on Nickel-55' Thiodisalicic Acid System

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55' thiodisalicic acid [hereafter abbreviated as TDSA] has been found to form complexes with a number of transition metal ions¹⁻⁵. A nickel-TDSA compound has been reported earlier^{2, 6}. Successful applications of this ligand has been made in medicine and industries^{7, 8}. In the present communication, the polarographic investigations of its complex with nickel using a dropping mercury electrode in acetate buffer (pH 4.8) has been described. The electrode reaction was found to be irreversible. Studies reveal that nickel forms 1:1 complex with TDSA in this medium. The transfer coefficient and forward rate constants of the electrode process have been evaluated.

Materials and Method

A fresh solution of 55' thiodisalicic acid (purity 99.7 per cent) was prepared in ethanol, and a stock solution of nickel sulphate (B.D.H. AnalaR) was prepared in double-distilled water by direct weighing.

Studies were carried out in 50 per cent ethanolic medium and acetate buffer [0.2M $\text{CH}_3\text{COOH} + 0.2\text{M}$ CH_3COONa] at pH 4.8. The ionic strength was kept constant at 0.2M by potassium nitrate which was used as supporting electrolyte. 0.005 per cent gelatin was added in the cell solution.

Polarographic measurements were made using a manual polarographic circuit as recommended by

Kolthoff and Lingane⁹. All potentials were measured against a Hume and Harris¹⁰ saturated calomel electrode (S.C.E.). Oxygen was removed from solution with a stream of oxygen-free nitrogen. An atmosphere of nitrogen was maintained over the cell during recording of the polarograms. All measurements were made at $25^\circ \pm 0.1^\circ \text{C}$.

The characteristics of the d.m.e. were $m=2.089$ mg./sce., $t = 3.60$ sec., $h = 36.4$ cm. and $m^{2/3} t^{1/6} = 2.023$ $\text{mg}^{2/3} \text{sec}^{-1/2}$

All pH measurements were made with a Leeds Northrup pH-meter fitted with a general purpose glass electrode.

Results and Discussion

Nickel (II) gives a well defined and diffusion control 2-electrons irreversible wave in acetate buffer. The $E_{1/2}$ at pH 4.8 is 0.960 volt vs S.C.E. On adding the ligand solution gradually, $E_{1/2}$ shows a shift towards more negative values (Table 1), indicating thereby a complex formation.

TABLE—CHARACTERISTICS OF NICKEL [$1 \times 10^{-3}\text{M}$] WAVE IN PRESENCE OF TDSA

Conc. of TDSA $\text{M} \times 10^3$	$E_{1/2}$ volts vs S.C.E.
5.0	0.970
10.0	0.985
15.0	1.005
20.0	1.017
25.0	1.022
30.0	1.027

* This study was carried out in the Chemistry Department, University of Allahabad, Allahabad, U.P.

† Manufactured by Eastern Organic Chemicals, Rochester, New York.

Plotting the potential of the dropping mercury electrode against $\log \frac{i}{i_d - i}$, a straight line was obtained in each case. The value of the reciprocal slope of these lines varied between 95 and 107 millivolts, which showed that the electrode reaction is irreversible. From the slopes of the log plot the value of transfer coefficient has been calculated to be 0.348.

The plot of $E_{\frac{1}{2}}$ (vs S.C.E.) against $\log [\text{TDSA}]$ was straight line (Fig. 1), having a slope of 0.076 volt.

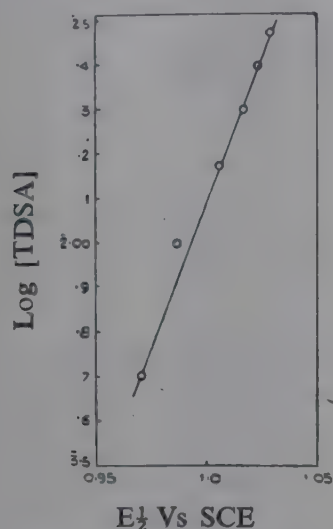


Fig. 1

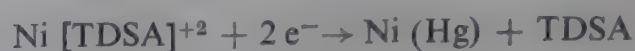
The value of this slope was used to calculate the kinetic parameters of the electrode process with the following equations given by Matsuda and Ayabe¹¹.

$$(E_{\frac{1}{2}})_c = \frac{0.591}{\alpha_n} \left[\frac{\log K^{\circ}_t}{D_N} f_N + \frac{1}{2} \log \eta - 0.053 - \log \frac{i_e}{i_d} - (N-p) \log f \times C_x \right] \dots\dots\dots (1)$$

where K°_t is the forward rate constant, D_N the diffusion coefficient of the complex in the solution and η the drop time at $E_{\frac{1}{2}}$.

From the slopes of the $E_{\frac{1}{2}} - \log [\text{TDSA}]$ plot, the value of $(N-p)$ comes out to be nearly one. This indi-

cates that the stoichiometry of the Ni-TDSA complex is 1 : 1 and the electrode reaction may be written as



[neglecting the charge contribution of TDSA]

The value of the forward rate constant (K°_t) of this reaction has been calculated from the above equation and is found to be $[4.02 \pm .05] \times 10^{-17}$.

Acknowledgements

The author is thankful to Dr. H. L. Nigam, Department of Chemistry, Allahabad University, Allahabad, and Dr. B. K. Banerjee, Superintendent P & D Division, for valuable discussions and keen interest in the work.

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CAPACITANCE LEVEL ALARM INSTRUMENT* for Solid/Liquid Level Detection

This instrument for solid/liquid level measurements and detection has been developed by the Instrumentation Department of Planning & Development Division, Fertilizer Corporation of India Ltd., and its complete know-how has already been sold to M/s Bestobell India Limited for its large-scale manufacture.

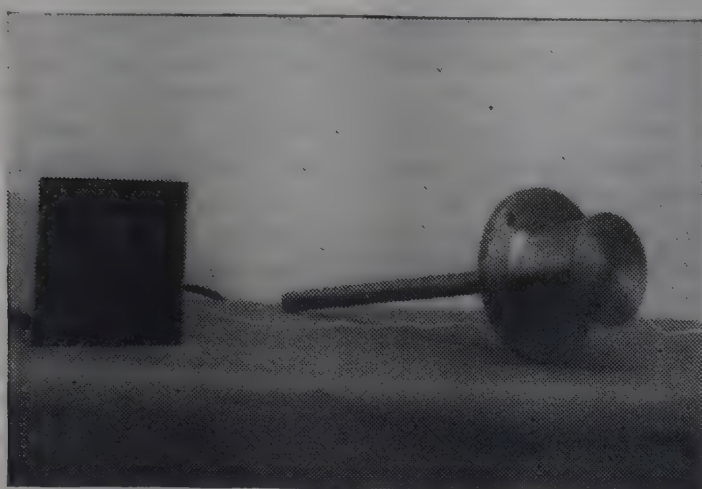
with respect to the solid/liquid level in the said container. The instrument consists of two parts—probe assembly and the indicating unit (see photograph). Probe assembly is located in the field and mounted directly on the vessel body while the indicating unit is kept far-off in the control room. An ordinary three core cable is needed to connect the probe assembly with the indicating unit. An oscillator-cum-detector is fitted in the probe head, whose state of oscillation depends upon the posi-

signal is transmitted to the indicating unit for the audio-visual indication for the change of the solid/liquid level in that vessel.

Application: It has very wide application in the industry for level monitoring and indication. It is a reliable instrument for solid level detection where other instruments are failing. It can be used for wide range of materials for level detection, such as : coal-powder or lumps ; granular solids like—fertilizer, wheat, sugar, etc. ; cement, raw ore, etc., as solid material ; water, acids, alkalies, oil, ammonia, petrol, alcohol, etc., as liquid and also applicable in many cases for slurries. In fact, it is a universal instrument in level measurements and applicable almost for all process materials.

It can also be used for detecting the interface level of liquids and change of liquid phase to solid phase of *vice versa*.

Special feature: It employs 100 per cent indigenous components. It is a very sensitive instrument and responds even to a 0.05 p.f. change of capacitance to the probe. Its high sensitivity makes it useful to mount the probe either in the vertical, inclined or horizontal direction. The indication unit can be taken about one kilometre or more far-off from the probe without affecting the overall performance. Indeed voltage has no effect on the performance of the instrument. Probe circuit is intrinsically safe and can be employed for hazardous areas.



Level Alarm—Capacitance Type : At right is the sensing probe which will be mounted on a tank/hopper for detecting solid/liquid level. At left is the visual indicator-cum-audible alarm. These units are connected by unshielded cable.

The instrument 'Capacitance Level Alarm' is a capacitance switch whose opening and closing state depends upon the proximity of the sensing probe in a vessel, hopper, tank, etc.,

tion of the level in the vessel. A change in the solid/liquid level in the vessel beyond a pre-fixed setting brings out a change in the state of the oscillator and corresponding

* Indian Patent No. 130459 (Inventors: G. P. Gupta and I. K. Suri, Planning and Development Division, Fertilizer Corporation of India Ltd., Sindri).

Utilization & Disposal of Industrial Wastes

A seminar on Utilization and Disposal of Urban and Industrial Wastes, organized by the Calcutta Regional Centre of the Indian Institute of Chemical Engineers, was held in the Jadavpur University Campus, Calcutta, on December 8-9, 1973. The following three papers were presented at the Seminar by the scientists of the Chemical Research Wing, Planning & Development Division, FCI, Ltd., Sindri: (1) Recovery of Fluorine from Phosphatic Acid Plant Effluent as Synthetic Fluorspar by G. S. Bhattacharyya, G. S. Roy, C. D. Banerjee, Suresh Singh and B. K. Dutta; (2) Removal of Ammonia Nitrogen from Nitrogenous Fertilizer Factory Wastes by G. S. Bhattacharyya, S. K. Bhattacharyya, G. S. Roy and B. K. Dutta; and (3) Removal of Fluorine and Phosphorous from Phosphatic Fertilizer Factory Wastes by G. S. Bhattacharyya, C. D. Banerjee, B. K. Dutta and G. S. Roy.

In the first paper a process for production of synthetic fluorspar (CaF_2) from the concentrated fluoride-bearing effluent as well as precipitated silica in phosphoric acid production has been discussed. In the first stage of the process, the filtered concentrated waste liquor containing hydrofluosilicic acid (H_2SiF_6) is reacted with ammonia where ammonium fluoride is formed with precipitation of silica, which is filtered out and dried at a suitable temperature. The filtrate is further reacted with a proper quantity of pure lime where calcium fluoride is precipitated. The calcium fluoride is filtered and dried. The ammonia is recovered from the filtrate. Both the stages of precipitation of silica and calcium fluoride formation require rigid control of reaction conditions. The calcium fluoride obtained by this process can be of 97 per cent purity and is equivalent to acid grade fluorspar. Fluorine recovery attained by the above process is about 92 per cent and silica recovery about 95 per cent.

In the second paper, the various processes for ammonia nitrogen removal, particularly those of practical applicability for treatment of nitrogenous industrial waste waters, have been discussed elaborately. At the present stage of technology of these processes, physico-chemical processes have a definite edge over the biological processes as far as treatment of highly concentrated ammonia nitrogenous waste is concerned. Biological processes such as nitrification-denitrification and algae uptake, though theoretically sound, would be impractical at the present moment for treating fertilizer waste waters containing high ammonia nitrogen. The nitrification-denitrification process demands very high power requirement for blowing air at the very high air/liquid ratio required in the nitrification stage and quite a high amount of easily oxidizable source of organic carbon in the denitrification stage. The algae uptake process is impractical as it requires very large land area, elaborate piping arrangement for diffusion of very high amount of CO_2 , about 50-60 per cent of which is lost and not utilized by algae. Of the physico-chemical processes, air-stripping at cooling tower type ammonia stripper may be applicable but the high air-to-liquid ratio for efficient removal of ammonia nitrogen would require very high power requirement which may prove a bottleneck at the present condition of power shortage in the country. Moreover, ammonia thus removed by air may cause air-pollution and ultimately return to the water course by directly dissolving in water or along with rains—thus having practically no gain. Ion-exchange by using suitable synthetic nuclear sulphonic cation-exchanger in the hydrogen form and recovery of ammonia from the regenerate waste as ammonium sulphate seems to be a practical proposition for removal of ammonia nitrogen (NH_4N) from nitrogenous fertilizer factory waste waters. Steam-stripping in a suitably designed still and recovery of the liberated ammo-

nia as ammonium sulphate in so-called saturators has also got practical applicability. The major cost factor in both the cases is steam, in the former for concentrating ammonium sulphate solution (12-15 per cent) and in the latter for both distillation of ammonia nitrogen and concentration of ammonium sulphate solution. It may be noted here that about 95-98 per cent of the total ammonia nitrogen pollution load in nitrogenous fertilizer factory waste water comes from ammonia processing or finished fertilizer salt section especially from the concentration and drying section. The volume of this ammoniacal waste from the salt section of a 1,000 te/day capacity nitrogenous fertilizer factory is only about 25-30 m³/hr with an ammonia content of 0.5 to 1 per cent. Proper segregation of this effluent and recovering NH_3 from this low volume highly concentrated ammoniacal waste by ion-exchange or steam stripping in distilling still should pose no serious problem in a modern fertilizer complex. The by-product ammonium sulphate, thus recovered, may not be economical when compared with the ammonium sulphate produced in a commercial plant but it would definitely be economical when considered from the view point of giving adequate and costly treatment demanded by other processes.

In the third paper, a process of removing fluorine and phosphorus-bearing acidic wastes from phosphatic fertilizer industries by a two-stage treatment with chalk and lime has been presented. In the first stage of the two-stage treatment system, the effluent is neutralized with by-product chalk to pH 3.5-4.0, allowing a reaction time of 30-40 min. with adequate agitation when about 85.90% of the influent fluorine is removed being precipitated as insoluble calcium fluoride but phosphorous removal at this stage is only marginal as the phosphoric acid is converted to soluble mono-calcium phosphate. The slurry from the first stage contains the residual fluorine and most of

the total phosphorus as mono-calcium phosphate. The slurry from the first stage containing the residual fluorine and most of the total phosphorus as mono-calcium phosphate is subjected to second stage lime treatment to pH 8.0-8.5 and reacted for

30-40 min. with adequate stirring as in the first stage. The mono-calcium phosphate is converted to calcium hydroxyapatite, which is highly insoluble and is precipitated along with most of the residual fluorine. Phosphorus and fluorine removal

attained at this stage is about 98-99 per cent. From a phosphatic fertilizer factory, waste containing 5,000 H_2SiF_6 (as F) and 1,025 mg./l. H_2PO_4 (as PO_4), fluorine and phosphorus was reduced to 10 and 5 mg./l. respectively by this process.

TECHNOLOGY

OFFER FOR EXCHANGE

This quarterly, TECHNOLOGY, is offered in exchange with other scientific and technical journals for mutual benefit. It is already being exchanged with about eighty journals—foreign and Indian. Editors of journals devoted to all branches of science and technology and particularly fertilizer technology, applied chemistry, chemical engineering, food technology, agronomy, agricultural chemistry, soil science, fuel technology, etc. may write to the Editor of TECHNOLOGY.

Conferences & Seminars

Coal-Based Fertilizer

Under the auspices of the Sindri Regional Centre of the Indian Institute of Chemical Engineers, a one-day seminar on coal-based fertilizer was held on March 17, 1974 in the Bihar Institute of Technology, Sindri to prepare a case for the speedy execution of a coal-based fertilizer project in Ramgarh area. In all 10 papers were presented.

Inaugurating the seminar, Sri O. P. Agarwal, General Manager, Planning and Development Division, FCI Ltd., said that our arguments in favour of coal-based fertilizer plants were purely on the consideration of self-reliance and availability of indigenous resources. Ten years ago the technological groups who mattered in framing the country's policy in respect to fertilizer technology felt the coal technology has become completely outmoded. But he said that the utility of a technology depended on circumstances and conditions prevailing in a particular country. If India had enough oil resources like Iran, it would not have been wise to suggest setting up of coal-based plants. Even as late as 1970 doubts were expressed about coal-based plants. But in view of abundant availability of coal in India, the economic viability of fertilizer plants based on coal should never have been a matter of dispute. Now, due to sudden rise in petroleum price people from all rostrums were talking of turning to coal.

Welcoming the delegates, Dr. K. P. Gupta, Director Bihar Institute of Technology, and Chairman of the Sindri Regional Centre of the I. Inst. Chem. Engrs. paid tribute to Dr. K. R. Chakravorty, the former Chairman and Managing Director FCI Ltd., for his foresight in championing the cause of coal-based fertilizer plants from about 10 years ago in order to survive as a nation with dignity and to work for self-reliance. With present scarcity and consequent increase of oil prices, conventional naphtha—feedstock for fertilizer plants—has ceased to maintain its economic balance.

Earlier, Dr. N. Singh read the Secretary's report and Prof. A. Bandopadhyay proposed a vote of thanks.

The afternoon technical session was inaugurated by Sri Dharamvir Sinha, Union Deputy Minister for In-

formation and Broadcasting, who was introduced by Sri R. K. Ghosh, General Manager FCI Ltd, Sindri Unit, and later welcomed by Dr. K. P. Gupta. In his inaugural speech, Sri Dharmavir Sinha said that a seminar like this should have been held at least 4 years earlier. He cautioned the scientists of tomorrow not to be led by fads and preferences in making important decisions on feedstock. In designing the future coal-based plants the planners should take into account the low grade coal available in the country.

Technical Session: The technical session held after the inauguration was chaired by Sri A. Dutt Majumdar, Chief Engineer (Design), P and D Division, FCI Ltd.

In the first paper,¹ Sri S. Y. Kekre (P & D Divn., FCI) highlighted the importance of the selection of raw material for the fertilizer industry for achieving self-sufficiency in food production. With the development of steam-hydrocarbon reformation at high pressure a number of fertilizer plants using naphtha are coming up in India. Subsequently, due to the expected shortage of naphtha, several projects based on partial oxidation of fuel oil and 3 large coal-based plants are now coming up. Considering the target for the installed capacity (7 million tons) of nitrogen fixed during the end of the 5th plan and the firms projects completed by that time a gap of 2.875 million tonnes has to be bridged. With the world-wide crisis for the crude oil and consequent steep rise in its price, coal has become very important to reduce our dependence on imported crude oil. Incidentally, there has been substantial development for direct coal gasification, which when combined with the single stream and integrated steam-intensive plants in large capacities and much lower cost of coal near the pit-head will be more attractive than naphtha/fuel oil gasification. They have discussed the following three main commercially important coal gasification processes: (i) fluidized bed gasification known as Winkler process (ii) fixed bed process, viz. Lurgi process, and (iii) entrain bed gasification, viz. by employing finely powdered coal in a co-current stream, known as Koppers-Totzek process.

The Winkler's process depends upon the interaction of a fixed and a fluidized bed of fine fuel of -16 mm. size with oxygen and steam. Highly reactive caking fuel, like lignite, is considered suitable for this type of gasifier which requires careful drying, grading and separation of fines from the feed to minimize losses of combustible rich materials from the product gases. A blast of oxygen and steam is passed through a fixed bed of graded fuel dried to below 8% moisture at a velocity such that the bed gives an appearance of a boiling system operating at a pressure slightly above atmosphere. The velocity of the blast is important; it should not be very much in excess, as underacted oxygen can cause explosion. A uniform mixture of oxygen and steam is very important to prevent slagging. The temperature of fuel bed is kept below 300°C . To eliminate the presence of some volatile matter, methane and unreacted carbon, a secondary blast of oxygen and steam can be introduced over the fluidized bed. The gas outlet temperature from the gasifier is around 900°C corresponding to ash fusion temperature (1000°C). Carbon efficiency is low (55%). A typical analysis of gas from brown coal is as follows (% v/v): CO_2 16-24, H_2 38-44, CO 27-42, CH_4 0.7-1.5, H_2S 0.5-1.5, N_2 0.5-1.5. The following 4 ammonia plants based on this process are in operation: Azot Gorazde, Yugoslavia (50 te/day NH_3); Stotelo Puertollano Works, Spain (140 te/day); Azot Sanajii Tas, Turkey (120 te/day); and Neyveli Lignite Corpr. (300 te/day). Some Winkler gasifiers have been installed in USSR, Bulgaria, E. Germany, etc.

The Lurgi gasification system works in the pressure range 25-40 kg./cm². A mixture of oxygen and steam is passed through a rotating grate at the bottom of a fixed bed of sized coal of size from 3 to 50 mm. The coal charge travels continuously downwards counter-current to the gasifying medium and is successfully dried, devolatilized and gasified. Ash is removed from the bottom by the rotating grate. The crude gas leaving the gasifier at $300-600^{\circ}\text{C}$ contains 9-10% CH_4 , and besides coal dust tar, oil, naphtha vapours and other hydrocarbons. Subsequently, the gas in wash cooler condenses heavy tar fractions and gas liquor; the tar fraction can be recycled back to the gasifier. The gas from the gasifier given the following analysis (% v/v): CO_2 28-30, C_nH_m 0.2-0.4, CO 18-21, H_2 37-43, CH_4 7-12, N_2 0.3-0.4 and H_2S , COS 0.2-0.4. Coal ranging from lignite to anthracite with ash content as high as 35-50% have been successfully gasified. Ash fusion characteristics, caking index, etc. influence the operation to a great extent.

Gasifier upto 3.7 m. diam. producing about 40,000 Nm³/h has been installed. The following ammonia synthesis plants use Lurgi process: Daud Khel, Pakistan (1956) 60 te/day; Nazu Fertilizer, Korea (1962) 150 te/day. The Sasol plant (S. Africa) has a hydrocarbon synthesis plant using this gasifier, the tail gases from which is processed to NH_3 .

The Koppers-Totzek process uses dust coal of fineness 90 per cent passing through 0.09 mm. and dried to 1% moisture blown through special burners along with oxygen and a little steam in a gasifying chamber (1600°C) from several ends at slightly above atmospheric pressure. Due to high temperature almost all the higher hydrocarbons are cracked to give a raw gas rich in H_2 (25-29%) and CO (52-57%) with very low methane (0.1%). Ash in molten stage is removed (sometimes mixed with a little limestone) and quenched in the gasifier bottom. Coal of wide range of quality and ash content can be gasified. This gasifier has a quick adaptability for a change in coal characteristics; it is usually preceded by a feed preparation plant. This plant can be scaled up for a raw gas capacity equivalent to 300 te/day NH_3 . The following Koppers plants have been built for the production of NH_3 : Tippi Oy Oulu Works, Finland (1950) 120 te/day; Nihon Siusokogyo Kaisha, Japan (1954) 120 te/d; Mac Moh Works, Thailand (1963) 100 te/day; Azot Sanajii Tas, Turkey (1966) 340 te; Nitrogen Chemicals Kafue, Zambia (1967) 100 te; Ptolemais Works, Greece (1969) 405 te.

The speaker then gave the details of the process schemes, adopted for the 3 large coal-based fertilizer plants, based on Kopper-Totzek process, using second grade low quality semi-bituminous coals (ash 18-30%) under installation at Talcher, Ramagundam and Korba.

The process-schemes adopted for the above 3 plants are single stream to the extent possible having high pressure steam for use in the turbines as major compressor drives in an integrated steam network, thereby reducing electric power load substantially. The gasification in one step gives a raw gas rich in CO and H_2 (with inert gases as low as 1 per cent) eminently suitable for processing in a conventional gas processing train, its quick adaptability with varying coal characteristics, ash content and ash melting point, simplicity of gasifier construction and type of its component and gas cleaning assembly with a wider scope of indigenization, possibility of raising steam in the waste heat boilers at high pressure, adop-

tion of conventional operations and catalysts in the subsequent purification train comparatively less maintenance, etc.

In selecting a process route for desulphurization in the purification train considerations have been given for a physical adsorption process against a chemical one. The authors have discussed in details the coal preparation, raw gas preparation and subsequent purification and the steam network.

In the second paper², the authors (BIT, Sindri) have examined the economic feasibility of all the different routes of manufacturing hydrogen for its ultimate use in synthesis gas manufacture in the Indian context, viz. from natural gas, steam-hydrocarbon process, steam-water gas process, electrolysis of water, steam-iron process, refinery off-gases and coke oven gas, etc. and finally came to the conclusion that the best alternative would be the direct gasification of coal. India has enough reserves of non-coking coal while those of crude oil are very meagre. With the development of the process technology of coal gasification using large capacity single steam units and steam-driven centrifugal compressors, the coal-based fertilizers will be cheaper than naphtha-based ones in the inland regions.

In the third paper³, J. N. Mahto (P & D Divn., FCI) has discussed the suitability of adopting the molecular sieve method of purifying industrial hydrogen. The molecular sieves are essentially synthetic zeolites having 3-dimensional network of pores containing water of hydration. Once this loosely packed water is removed the sieves adsorb the polar molecules of CO, CO₂, etc. and the straight molecules of gases having molecular diameter less than or equal to 4 Å. When the gas mixture for CO shift conversion is passed through the bed, the unadsorbed gas essentially hydrogen emerge in the pore form. The bed can be regenerated by raising the temperature of the bed or by passing a purge gas or by both. By having at least 3 beds in operation, this process can be made continuous.

The technique for hydrogen purification going to be adopted in some of new fertilizer plants is the Rectisol process, wherein the impurities, like CO₂, H₂S, organic sulphur compounds, HCN, etc., are removed by physical absorption in methanol at relatively lower pressure. CO₂ and H₂S are highly soluble in methanol.

The molecular sieve process has all the advantages that Rectisol process has. In addition, it has the following advantages over the latter : (i) it requires less number of equipments, operating conditions being either room temperature with high pressure or high temperature and pressure; (ii) the sieves would be available indigenously and therefore cheaper. The speaker suggested that molecular sieve method should be developed as this will save a lot of foreign exchange.

In the fourth paper⁴, S. Chandra and R. K. Dubey (BIT) have advocated the case for gasifying inferior non-coking coal which is abundant in India, for the manufacture of synthesis gas for the ultimate manufacture of nitrogenous fertilizers, as the sources of other feedstocks, viz. natural gas and crude oil, are very limited. After giving an exposition of the chemistry of the gasification process, the authors discussed the following different coal gasification processes indicating their advantages and disadvantages :
1. **Fixed bed processes** (i) Lurgi Process, (ii) Luna Würth process and (iii) Thyssen Galocsy process ;
2. **Suspended fuel in a gas** : (i) Fluidized system—Winkler process (ii) Fully entrained system—Koppers-Totzek process (iii) Cyclone and Vortex gasifier—Rummel slag bath gasifier. Koppers-Totzek process is superior to Winkler's because of its (i) adaptability to wider varieties of fuel, (ii) less oxygen consumption and (iii) its 90% carbon conversion efficiency against that of Winkler's 69%. The Rummel slag bath gasifier is of interest because it offers (i) a wide choice of fuel (ii) high throughput, (iii) optimum gas composition (iv) high carbon, gasification and thermal efficiencies and (v) flexibility in operation.

The formation of tar, oil and liquor and presence of methane in raw gas always create problem of their disposal. The use of oxygen in the gasification of coal requires expensive plants and is uneconomical in smaller units. Research is, therefore, at present directed in developing processes for production of gas without use of oxygen. There are schemes which involve external heating, recycling of a heat carrier a recycle gas. Besides these, studies have also been directed towards utilization of heat from atomic reactors for endothermic steam : carbon reactions.

In the fifth paper⁵, T. K. Jaiswal and B. Chatterjee (P & D Divn., FCI) have discussed the problem of changing over of the existing naphtha-based ammonia plants because of the world wide oil crisis to coal-based ones. So to replace the naphtha reformation

plant, a gas similar to the reformed gas is required. Of the 3 major coal gasification processes, viz. Winkler, Lurgi pressure gasification and Koppers—Totzek, the authors recommend the Lurgi process as it gives a raw synthesis gas similar in composition to that available from naphtha reformation plants, so that there is least modification in the purification stream. This will require least capital investment and least time to bring about the change-over. The methane content in the gas available from Lurgi gasification is nearly the same as that obtained from primary reformer.

TABLE 1—TYPICAL ANALYSIS OF GAS FROM COAL GASIFICATION

Components	Winkler Gasification	Lurgi Pressure Gasification	Kopper-Totzek Gasification
H ₂	38-44 % v/v	37-43 % v/v	25-29 % v/v
CO	27-42 % v/v	18-21 % v/v	55-57 % v/v
CO ₂	16-24 % v/v	28-32 % v/v	11-15 % v/v
CH ₄	0.7-2.5 % v/v	7-12 % v/v	0.1-0.2 % v/v
C ₂ H ₆	—	0.2-0.4 % v/v	—
N ₂ , Argon	0.5-1.5 % v/v	0.3-0.4 % v/v	1.0-3.0 % v/v
H ₂ S COS	0.5-1.5 % v/v	0.2-0.4 % v/v	0.2-0.4 % v/v

The gas available from Lurgi process is nearly the same as that obtained from the primary reformer and therefore it can be reformed in the existing secondary reformer in presence of air or oxygen-enriched air. As the Lurgi gasifiers operate under pressure the coal gasification pressure can be adjusted to suit the pressure in the purification stream. The gas from Lurgi gasifier contains H₂S and COS and hence a new desulphurization section has to be installed and the sulphur content of the gas to be brought down to about 0.1 ppm, which is the permissible sulphur tolerance of L.T. shift conversion catalyst. As the CO and CO₂ content in Lurgi gas is more than that in naphtha reformed gas, so the high and low temperature shift conversion and decarbonation sections will need modification and expansion. The methanation section need not require modification or expansion as the composition of gas exit decarbonation section will be nearly the same as that obtained in case of naphtha reformation. If nitrogen in desired quantity cannot be introduced in the secondary reformer this can be done at the exit of the methanation section to have H₂ and N₂ in the ratio 3 : 1 in the synthesis gas. An air separation plant has to be installed to supply oxygen.

In order to replace fuel oil-based partial oxidation plant by coal-based plant, a coal gasification process

which gives gas having high H₂ and CO and low CH₄ should be chosen so that the gas can be processed in the subsequent sections with least modification. The gas available from Koppers-Totzek process is the best to replace the gas obtained from fuel oil gasification, but as Koppers-Totzek process operates at near atmosphere pressure the gas has to be compressed to a pressure at which the purification stream operates. The steps suggested by the authors are as follows: The Koppers-Totzek gas to be first compressed in a turbine-driven centrifugal compressor and a part of it is taken to shift conversion of the gas is so adjusted that after mixing it with the balance amount of Koppers-Totzek gas, the final gas composition comes to near about that obtained from fuel oil partial oxidation plant. The mixed gas is then processed in the existing purification stream. The existing purification sections, viz. Rectisol desulphurization and decarbonation sections, shift conversion and liquid nitrogen sections, may not need any modification. The shift conversion and decarbonation sections for treating a part of Koppers-Totzek gas will have to be installed. The proposed decarbonation section may use any conventional process, viz. Benfield process for CO₂ removal. As the oxygen requirement for coal gasification is more than that required for fuel oil partial oxidation process, so the air separation will have to be expanded. Also the power, cooling water and steam requirements after change over to coal gasification process will be more and these facilities will have to be expanded. Table 2 gives a comparative requirement before and after changeover.

TABLE 2—UTILITIES CONSUMPTION INDEX FOR AMMONIA PLANT

	Power (kWh/H)	Cooling water in circulation	Service boiler capacity
Fuel oil—based ammonia plant	100	100	100
After changeover to coal-based ammonia plant	200	147	138

The authors have discussed the effects of the changeover of naphtha reformation and fuel oil partial oxidation to Lurgi pressure gasification and Koppers-Totzek process respectively on the stream network.

In the next paper⁶, V. K. Singh and A. K. Sinha (BIT) have dealt recovery of NH_3 and H_2S from coke oven gas and preparation of ammonium sulphate therefrom after converting H_2S to H_2SO_4 . Of the 3 processes for recovering ammonia, viz. direct, indirect and semi-direct, the semi-direct process is most widely used although direct method has the smallest investment and operating cost and lowest steam consumption but having a great disadvantage, viz. presence of an undesirable impurity in the product. In the semi-process the cost for steam, labour and capital repayment are lower than that in the direct process, while it gives ammonia recovery higher at least by 5% ; in spite of high power consumption semi-direct process is much easy to operate since the saturator conditions are much less critical and thus economical. The saturator design and operating conditions, particularly the temperature and the acidity, have greatest bearing on the quality of the product. Theoretical acidity should be kept low at 2-3 per cent but it is actually maintained at 5-7%.

The coke oven gas contains 300-500 grains H_2S per 100 SCF; the latter is generally removed by use of oxide boxes—large steel chambers or towers containing porous beds of an active hydrated iron oxide and generally 4 or more such boxes operated in series.

However, a better method is the Sea-board process and its improved version the vacuum carbonate process, which are most economical ; the use of vacuum reduces the steam requirement to about one-sixth. The authors have described the vacuum process which is as follows: The impure gas is contacted with dilute sodium carbonate in packed counter-current absorber and the net solution is passed to the top of the rectified column where it is regenerated by vacuum distillation. The regenerated solution is then pumped from the bottom of the rectifier through a solution cooler and back to the absorber. The gases from the top of the rectifier containing H_2S , CH_4 , CO , and water vapour are passed through condensers and vacuum pump system. The heat required for activation is provided by flow-pressure steam in a reboiler at the base of the actifier.

In the light of the present energy crisis, attention is now diverted to other energy sources, such as coal, nuclear power, solar energy, etc. So the countries with large reserves of coal have started evincing a new interest in coal. In India too, FCI Ltd. many

years ago drew the attention of the Government to the risk involved in tying up a substantial part of country's productive capacity in a crucial input, like fertilizers, to a raw material, like naphtha, which would involve direct or indirect imports and consequently a recurring drain of foreign exchange and the supplies of which could be subject to uncertainties, political and economic. FCI also tried to convince that after making provision for utilization in high value petrochemicals, the availability of straight-run naphtha in the country could not support creation of naphtha-based fertilizer capacity. Now, it has come to such a pass that not only indigenous naphtha can not support the total production capacity of about 2-4 million tonnes already created but even the import has been extremely difficult on account of international shortage.

Sri A. K. Bhaduri⁷ presented the case for a coal-based fertilizer plant north of Gidí area in the South Karanpura coalfield (S. Bihar). This coalfield has sufficient coal reserves potential to meet the requirements of a fertilizer plant. The source of water is nearby and the Bihar State Electricity Board has assured supply of 60 MW electricity. If washed coal from NCDC's Gidi washery is made available for processing, this will be an added advantage.

This project is envisaged to produce about 0.5 million tonnes of urea (46% N) per year from the complex comprising a 900 te/day NH_3 and 1500 te/day of urea. The annual requirement of coal (20-22% ash) works out to be about 600,000 tonnes for gasification for synthesis gas. The requirement of coal (30-35% ash) for steam generation works out to be about 45,000 te/yr. The water requirement would be 15 mil. gallons/day, while electricity requirements work as out to a load of about 50 megawatts ; in addition, about 200,000 te/yr of limestone would be required for ash removal. The authors have envisaged an investment of about Rs. 157 crores inclusive of requirements towards main plants, offsites housing colony and working capital (Tables 3 & 4).

In the next paper⁸, the author, A. K. Sen (BIT), described the coal gasification chemistry and discussed the gasification techniques. He briefly dealt at the end some of the newer developments of this technology, like (i) gasification of coal by steam itself or by steam and air for getting the requirement of an oxygen plant, (ii) hydrogasification, i.e. gasification by steam and hydrogen under pressure, underground gasification of coal, etc.

TABLE 3—TOTAL CAPITAL OUTLAY FOR GIDI FERTILIZER PROJECT

(Rs. in lakhs)				
Sl. No.	Item	F.C.	I.C.	Total
MAIN PLANTS				
1.	Ammonia Plant	1574	5922	7496
2.	Urea Plant	09	919	1728
3.	Product Handling	—	138	138
4.	Steam Generation	12	1041	1053
5.	Cooling Tower	—	99	99
6.	Land & Land Development	—	61	61
	Sub-total	2395	8180	10575
OFFSITES				
1.	Power Supply & Distribution	6	211	217
2.	Water Treatment and Distribution	3	149	151
3.	Auxiliary Services	21	116	137
4.	Transport Facilities	—	136	136
5.	General Welfare Facilities	—	23	23
6.	Effluent Treatment and Disposal	6	29	35
7.	Earthmoving, Construction and Coal Handling Equipment	3	91	94
8.	Non-plant Buildings	—	80	80
9.	Departmental Charges	3	300	303
10.	Coal Conveying System	—	454	454
	Total Manufacturing Facilities	2437	9769	12206
11.	Contingency & Escalation	244	977	1221
12.	Township	—	350	350
13.	Initial Working Capital and Spares	230	1014	1244
14.	Financing Charges	—	686	686
	Total Capital Outlay	2911	12796	15707

According to Dr. S. K. Singh⁹ (BIT), out of 1.30 billion tonnes of coal deposit in India 49 per cent is available in Bihar, so the Government should expedite the execution of the Ramgarh fertilizer project in S. Bihar. As the daily coal consumption for a 900 te/day ammonia plant would be as high as 7200 te, so the distance between the coal mine and the gasification plant should be as less as possible. He warned against the habit of depending too much on foreign collaboration as the Indians, since the establishment of Sindri fertilizer factory, have gained enough experience and developed sufficient know-how on fertilizer technology. He appealed to the Government to encourage and entrust the Planning & Development Division of FCI Ltd. for conducting process development work on laboratory and pilot plant scale and finally design and erect large scale fertilizer plants.

In the last paper¹⁰, the authors (BIT) have presented the current position of naphtha supply, outlined the different routes for ammonia synthesis and finally put forward the arguments in favour of establishing a coal-based fertilizer plant near Ramgarh (S. Bihar), where large reserves of non-coking coal are available. This area also has dams on the tributaries of Damodar river. So they have preferred this area over Gidi, where the supply of water is not copious but sufficient coal is available. They have therefore sug-

TABLE 4—COST OF PRODUCTION OF GIDI PROJECT

Sl. No.	Item	Unit	Unit Rate, Rs.	Annual Consumption	Annual Cost, Rs. lakhs
1. RAW MATERIALS					
(a)	Coal for Process	Te	47.68	5.80×10^5	277.00
(b)	Limestone	Te	50.00	0.168×10^5	8.40
2. UTILITIES					
(a)	Coal for steam generation	Te	41.50	4.75×10^5	197.20
(b)	Power	MW	93.10	3.84×10^5	358.00
(c)	Water	MG	400.00	4840	19.33
(d)	Consumable stores	—	—	—	53.54
(e)	Labour and Overheads	—	—	—	90.00
(f)	Maintenance Material	—	—	—	366.00
(g)	Insurance and Taxes	—	—	—	61.00
(h)	Bags	No.	Rs. 50/- te product	—	248.00
(i)	General Expenses and Contingencies	—	—	—	83.92
	ANNUAL WORKS COST				1762.39
	Interest on working capital @ 11%				58.86
	Depreciation				1200.13
	TOTAL ANNUAL COST OF OPERATION				3021.38
	Annual Production			4,95,000 te	
	Cost of Production of Urea				Rs. 610.38/te

gested the location of the plant in Ramgarh, with coal being transported from Gidi either by ropeway or in a pipeline. In this connexion the authors have aptly quoted Dr. K. R. Chakravorty from a seminar arranged several years ago at Bombay by the Indian Chemical Manufacturers' Association, which had prepared a case (blue print) for a naphtha-based fertilizer plants against coal-based ones.

'Your study definitely shows that not only in terms of capital cost but even in production cost, coal as a feedstock for fertilizers will prove definitely more expensive and therefore must be ruled out. Sir, I submit that it is definitely not our conclusion. We have carried out a long analysis and the Government have scrutinized these for years and they have decided about the coal-based projects and 3 projects have been cleared.

While one considers the comparative economics, I admit that an imported crude oil plant may be cheaper in capital investment and it may also be cheaper in cost of production than coal-based plants. But if it is a coal-based plant there is no foreign exchange element; we are not dependent on other countries for feedstocks which may be stopped in times of hostilities.

Secondly, in discussing the required foreign exchange on the basis of which the calculation is made that one thing is cheaper or costlier than the other, the real value of the foreign exchange must be taken into account. What is the absolute cost of one dollar in terms of rupees which is called the shadow cost. We all know that it is of the order of Rs. 12 or 13. This means that an expenditure of a dollar in recurring expenses or in first investment will be in terms of rupees more than 1.5 times. Therefore, if you take into account all these in your costing, it will reveal what is cheaper and what is costlier in the best interests of the country.

We do not believe that in any and every place coal-based fertilizer is an economic proposition. Just as

naphtha-based plants or natural gas-based plants also have an optimum location where only they can yield economic production so also coal-based plants have some prerequisites. First of all availability of coal must be ensured, the continuous supply of one quality only. Only in those places can coal-based plants be successful. Next, there should not be any transport involved in the raw material. The distribution of the finished fertilizer should be such that the distance covered is minimum. Then the utilities required, viz. steam, electricity and cooling water, must be available at site at minimum cost. Under these conditions only we recommended a coal-based plant. Under these conditions, if you take a naphtha-based plant for comparison, you will find that it can not compete. For Korba, Ramagundam and Talcher, we have submitted project reports and project estimates and the cost of production of coal-based units compared with naphtha-based units. All these we have submitted to the Government and they after studying have accepted them'.

The authors have given the salient features of the FCI's Ramagundam coal-based project, as an example.

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World Fertilizer Situation and Ammonia Production Based on Heavy Fractions

A 2-day national seminar was organized by the Fertilizer Association of India during Dec. 14-15, 1973

in New Delhi, the first day being devoted to world fertilizer situation in the seventies and second on

technical and economic aspects of production of ammonia based on heavy fractions of petroleum and feedstocks.

World Fertilizer Situation in the Seventies

Inaugurating the first day's seminar, Sri Shah Nawaz Khan, Union Minister of State of Petroleum and Chemicals, mentioned the international oil situation causing large increases in fertilizer feedstocks' prices and cut-backs in their availability. He pointed out the drastic steps taken by the Government of India at curbing consumption of petroleum products. Availability and pricing of rock phosphate and phosphoric acid and the sharp rise in shipping rates are other important factors with serious impact on domestic availability of fertilizers. Any capacity now taken up for implementation would take 3 years for completion. The present installed capacity of 1.634 mil. tes of nitrogen, though based on a range of feedstocks, leans heavily on naphtha. In 1973-74 the anticipated production of 1.12 mil. tes of nitrogen may consume around 1.4 mil. tes of naphtha. There are several projects under implementation to supplement nitrogen capacity which on completion would increase the installed capacity to about 4.16 mil tes of nitrogen. Of the additional capacity under implementation amounting to 2.53 mil. tes, about 0.97 mil. te would be based on naphtha. But the Government have now decided in favour of diversification of feedstocks; the plants at Kalol (Gujarat) and Namrup (Assam) under construction are based on natural gas, while the projects (under implementation) at Haldia, Nangal and Sindri are based on heavier petroleum fractions and the large fertilizer plants at Talcher, Ramagundam and Korba will base on non-coking coals.

Sri Khan further stated that our plans for further expansion during 5th plan period envisage an installed capacity of about 7.0 mil. tes, a large part of which may become operative only by the end of the 5th plan period. The additional capacity may have to be based mainly on the use of heavier petroleum fractions for the production of ammonia.

Regarding phosphatic fertilizer industry which is completely dependent on imported rock phosphate and sulphur, Sri Khan stated that schemes are under consideration for utilization of the Udaipur rock phosphate and pyrites deposits at Saladipura (Rajasthan). He also pointed out that the Government have decided to waive the entire excise duty on fuel oil to be used as feedstock in fertilizer production. The

recent upward revision in the pricing of urea would also improve the profitability of fuel oil-based fertilizer production. With the possible cut-back in the availability of fertilizers from import, efforts have to be intensified to increase domestic production by way of improving utilization of existing capacities and expediting completion of projects under construction.

In proposing a vote of thanks to Sri Shah Nawaz Khan, Dr. S. K. Mukherjee, Vice-Chairman FAI and Director FCI Ltd., pinpointed the four major problems of the fertilizer industry, viz. (i) choice of feedstock to support our expanding industry; (ii) rapid building up of the industry with active participation of all sectors of industrial economy on a pragmatic approach on costs and prices in the national interests; (iii) take note of the rapidly changing position of supply of feedstock, fertilizer raw materials and fertilizers in the international scene and to the appropriate measures to adapt ourselves to the changing situation; and (iv) evolve an effective and suitable education, promotion and distribution system to make the best use of the limited availability fertilizers. Today there are no other options but to quickly launch at least 5 major additional coal-based projects for the production of 1-1.5 mil. tonnes of nitrogen. 8 projects, that have been approved or are under construction, based on heavy petroleum residues, would contribute nearly 1.7 mil. tes of nitrogen. 7 major projects in operation, based on naphtha are contributing to 1,000,000 tes of nitrogen; 4 more would come into commercial production during 1974/early 1975, contributing to an additional 600,000 tes and 2 more the year after, contributing additional 400,000 tes. Thus, 1.8 mil. tes based on naphtha and 1.7 mil. tes based on heavy petroleum residues are to be provided continuously with feedstocks based on crude petroleum. Considerable tightening in disciplining the demands of other sectors of economy using petroleum products would be required to sustain this capacity already built in the crucial field of fertilizers.

In the lead paper,¹ P. P. Agarwal, Secretary, Ministry of Supply, Government of India, stated that although food production world wide has increased in recent years, it has still not kept pace with growth in population. Of the projected increase of 856 millions in world population, the developing countries would alone account for 742 millions. The latter countries have, therefore, to provide for this additional population, which is not a small problem.

1. Lead Paper by P. P. Agarwal.

In India fertilizer consumption has been doubling every 4 to 5 years, and although domestic production has been rising it has always lagged behind the requirements, thereby making imports necessary. India today is the second largest importer of fertilizers. As against the existing production of nitrogen of 1.85 mil. tes, it is expected to go upto 4 mil. tes in 1978-79; similarly, production of phosphate is expected upto 1.2 mil. tes from 0.57 mil. Even these are far below the targets of consumption. Apart from the shortages there has been no control on prices and these have been on the increase practically every month. He urged that the Government and the industry in the producing countries should consider seriously fixing prices only in relation to the cost of production and reasonable returns and plan production on a global basis. He narrated the following points presented by India at the FAO meeting held in Rome in Oct. 22-24, 1973: (i) to assist in pre-investment studies and investment decisions to augment world-wide availability of fertilizers; (ii) to bring together countries which have cheap fertilizer raw materials and those having assured markets and assist in setting up joint ventures; (iii) to provide financial assistance through World Bank and technical assistance through UNIDO to get up such ventures; (iv) to undertake fund studies to upgrade fertilizer technology for increased productivity in fertilizer plants and finance research aiming at more efficient use of fertilizers; (v) to build a buffer stock (vi) to arrange aid for developing countries from the developed countries/world organizations in the form of fertilizers and foreign exchange to purchase fertilizers; (vii) to suggest ways and means to maintain prices at an equitable level.

In looking forward to the expansion of fertilizer capacity in the Middle East as they have natural gas and oil, Sri Agarwal appealed to the Middle East countries to exploit the use of the above two feedstocks and encourage other countries to set up new plants for which they should guarantee the supply the basic raw materials for a number of years.

In the second paper², Prof. Raymond Ewell of USA estimated that the present world-wide shortage of fertilizer will continue for an indefinite period, the reason being that investment capital to expand fertilizer industry will not be forth-coming with increasing demand for food and fertilizer generated by 75

million more people each year. The annual capital requirement at present is estimated at \$8,000 million which will increase to \$12,000/yr by 1980.

Technical manpower may be another limiting factor. The acute shortage for both nitrogen and phosphate fertilizers will continue for many years although the shortage for phosphate may be somewhat alleviated after 3-4 years by new production facilities. Most of the new nitrogen capacity will be in USSR, Eastern Europe, India, China and Latin America; of these countries, India and China will not have any surplus for sale, but USSR, Eastern Europe and Venezuela should become more important sellers of nitrogen fertilizers. According to Ewell², limitation of investment capital is likely to be the principal factor limiting the future development of the world fertilizer industry. New nitrogen fertilizer plants now under construction are estimated to increase the existing world capacity by 6 per cent during 1973-1975 compared with increase in nitrogen consumption of 9 per cent/yr during 1967-72. World fertilizer consumption is forecast at 94.1, 123.6 and 155.4 mil. tons of nutrients in 1975, '80 & '85, compared with 72.1 mil. tons actual consumption in 1971-72. According to Ewell, some of the large deficit countries, like China, India, Turkey, Suba and Egypt, will probably never be able to achieve self-sufficiency in fertilizer because of insufficient financial and material resources.

In a brief paper³, E. Bahari of Shahpur Chemicals Co. Teheran, made some observations on the productivity in fertilizer industry. 80 per cent as capacity utilization in fertilizer plants as a world average would be a good achievement. But the difference between the shortage today and surplus could be accounted for by the 20 per cent of the unutilized capacity as the difference between glut and shortage is about 10 per cent. According to the speaker, the reduction in capacity utilization is due to shortage of trained personnel in the field and therefore investment of money and time in training people in the industry would fetch handsome rewards. Additional investment is also needed to overcome the shortages.

The reasons for the current shortage of sulphur, according to J. M. Lancaster⁴ of British Sulphur Corporation, are different from those in the past. Previously the booms and slumps in sulphur market were generated by a shortage or surplus in production

2. Estimates of Fertilizer Production Consumption in 1980 and 1985 by Raymond Ewell.

3. Complex Fertilizer Production in Persian Gulf Area by E. Bahari.

4. Outlook on Sulphur Availability by J. N. Lancaster.

capacity. Usually, shortage of production capacity was engendered by a preceding period of low prices ; during this period the primary producers, mainly in USA and Mexico, were not able to invest adequately to meet the rising demand which inevitably followed. Essentially these period of booms and slumps were limited in time and the price fluctuations were within an acceptable parameters.

Today's shortage is not generated by a shortage of capacity ; in fact world produces 3 mil. tes. of sulphur more than it consumes because (i) legislation brought about by environment and antipollution lobbyists has prevented movement of sulphur from vats (jeep in Canada) ; (ii) transportation facilities at Vancouver—the only port in Canada available—for export of sulphur from Canada are inadequate. Then there is a limitation of shipping capacity for moving liquid sulphur. Upto 1975 the industry is left with a narrow margin and even that on the assumption sulphur producers produce to the maximum capacity. Surpluses that may be generated in E. Europe and USSR may go to Western world markets which are in short supply. It is necessary that producers and consumers of sulphur evolve a joint policy to avoid shortages of this vital raw material and fluctuations in its price.

Europe holds the key to the world fertilizer supply position. During 1971-72 West and East Europe taken together accounted for 41-44 mil. tonnes of nutrients out of the world production of 76.67 mil. tes of nutrients, i.e. over 54 per cent, whereas the population is only 18.5 per cent of the total world population. European production of nitrogen exceeded 18 mil. tes during 1971-72 accounting slightly more than 50 cent of world production of around 35 mil. tes. According to S. Ramachandran⁵, Chairman, MMTC, one outstanding development has been the emergence of E. Europe the world leader of nitrogen—its production exceeding 9 mil. tonnes in 1971-72 and from 1968-69 to 1971-72 this growth has been 43 per cent against western Europe's 4 per cent. The eastern block after servicing the deficit socialist countries has a surplus of over 1.4 mil. tes to spare for meeting the demands of the developing countries as well as of the western countries, like Italy. He gave a review of the fertilizer situation in some of the leading West European countries.

5. World Fertilizer Situation in the Seventies: European Scene by S. Ramachandran, Chairman, The Mineral & Metals Trading Corpr. of India Ltd., New Delhi.

In Italy nitrogen production is dominated by Government owned giants, viz. ANIC SpA and Montedison SPA, which have kept down the fertilizer prices in face of increasing production cost and wage level ; they have also kept loss-making units from being shut-down and bogged down further bold investment. In W. Germany imports have increased despite higher domestic production of 1.5 mil. tes of nitrogen, as fertilizer consumption increased at an annual rate of 6.2 per cent from 0.6 to 1.1 mil. tes of nitrogen. Obsessed with higher labour costs, new expansions in fertilizer production have been put off.

In Holland, with the exception of one ammonia plant, the nitrogenous fertilizer industry is based on natural gas. After home delivery they export 50-70 per cent of their nitrogen production (0.6 mil. tes in 1970-71). Ammonia capacity is around 2.2 mil. tes of nitrogen and they export their entire urea. In Austria, where the fertilizer industry is dominated by the state-owned Oesterreichische Stickstoffwerke AG, CAN is the major material used for the domestic consumption with complex fertilizer gaining ground of late ; it was an important nitrogenous fertilizer exporter during fifties.

The French fertilizer industry underwent a modest reorganization and consolidation in the sixties through mergers of the earlier fragmented structure and the State still continues to have a good hold on the industry through the formation of APC. France still imports high grade ammonium nitrate from Rumania, Bulgaria, etc.

In short, West European countries have been trying to sell their own high most fertilizers to the third world replacing part of their domestic requirements by cheaper fertilizers from E. Europe. During early 60s fertilizer industry, especially in the developed countries, attracted huge investment and fertilizer consumption was confined mainly to the developed countries, but these countries realized that their future potential market is in Asia, still undeveloped. So they offered inducements to developing countries by way of consortium and bilateral credits and by financing fertilizer promotion activities. By the middle of sixties countries, like India, became fertilizer conscious for increasing food production and by early seventies the prevailing surplus stock was disposed of giving rise to increase of price rise which continued because of (i) surging demand from developing countries ; (ii) in many such countries the production programmes did not proceed on targetted

schedules while consumption demand could not be held in check; (iii) dollar devaluation, awakening against pollution, world wide food shortage, further currency realignment culminating in second devaluation of dollar and finally the present oil crisis, causing several-fold increase in the price of naphtha, fuel oil and threat of curtailment of oil supplies from the Middle East. Thus, while demand for fertilizers is likely to continue unabated, the picture of further capacity creation is dismal.

In the developing countries the gap between the consumption and production of nitrogenous fertilizers is likely to grow from the current 3-4 mil. tes to nearly 5 mil. tes in 1975-76 continuing upto 1980-81. With increasing cost of plants and raw materials, the production programmes of the developing countries are likely to get tardier. Under these circumstances, the present supply of 2-2.5 mil. tes from Europe should be expected to increase to 4-5 mil. tes and stay through 1980-81, which means that capacity should increase by at least 15 per cent more.

As a result of phenomenal increase in production of nitrogen during the last 4 years, East Europe has emerged as the world leader. There are huge expansions in USSR, Poland and Rumania. USSR has concluded a \$8 bil. deal with an American company and a smaller deal with a W. European company for construction of fertilizer plants. They propose to double the production of nitrogen (from 5.3 to 10.6 m. tes) and potassic (from 4.5 to 9.0 mil. tes) fertilizers and treble that of phosphatic (from 3.8 to 14.4) fertilizers by 1980.

W. Europe is deficient in phosphatic fertilizers and the outlook for their expansion is also not bright, whereas E. Europe is fast gearing up its plans as it is relatively better poised to take the lead with Polish sulphur and imported rock phosphates from USA and N. Africa. USA has changed itself from exporter of rock phosphate to a manufacturer of diammonium phosphate with expanding phosphoric acid production.

Potash production is confined to France, W. Germany, Italy, Spain, GDR and USSR. The prices of nitrogenous as well as phosphate fertilizers have increase manifold with unprecedented freight levels, so much so that the developing countries can ill-afford to import fertilizers at such prices. An *ad hoc* inter-governmental consultation on fertilizer held on Nov. 5-9, 1973 decided to establish a commission on fertilizers with a view to promote the expansion

of production to meet the estimated demand, with special attention to the expansion of production in developing countries, whenever feasible.

Steep increases in export prices of fertilizers have created serious implications for developing countries, which are heavily dependent on imports. They can ill-afford the financial resources needed to cushion the effect of rising prices on their own farmers and to cope with the increased foreign exchange costs of the imports. In their paper, A. Robinson and K. L. C. Windridge⁶ of International Superphosphate & Compound Manufacturers' Association, London, have divided the developed countries into 3 groups, viz. western Europe, eastern Europe and N. America, each of which consumes 14-20 mil. tes of nutrients; they have classed all the developing countries as an integral group of which India accounts for 1/6 consumption of this group. The distinguishing features of the developing countries are (i) the extremely low use of phosphates and potash in relation to nitrogen and (ii) their general dependence on imports which in the case of phosphates is about one-quarter of their total requirement. With regard to nitrogen, western Europe and Japan are each net exporters of about 1.2 mil. tes although gross exports from W. Europe are twice this figure. E. Europe from particularly nothing 5 years ago, now exports about 1 mil. tes.

Regarding phosphate, USA, Morocco and USSR dominate world supplies, representing 80 per cent of the phosphate fertilizer consumption of the world. Canada now dominates the world potash scene with eastern Europe the next largest net exporter, whereas W. Europe has changed from a net exporter to an importer. In fact W. Europe is now in deficit for every fertilizer raw material and intermediate; it is receiving increasing quantities of nitrogen from eastern Europe.

Western Europe has also been importing about 200,000 tes of P_2O_5 every year from America as TSP and DAP. Then there are factors, like rising cost of capital, plant raw materials, frequent increase in freight rate and the effect of over-capacity during 1967-71, which have discouraged new plant investment. However, the engineering firms are busy with contracts for erecting ammonia plants in China, E. Europe and various developing countries. In compound fertilizers too the W. European exporters have maintained the ground.

6. Position of Western Europe and the Prospects for World Phosphoric Acid Industry by A. Robinson and K. L. C. Windridge.

In the next paper⁷, Jose A. Alvarez Ercillan of Madrid has described the characteristics of the phosphate rock deposits of Spanish Sahara and the development and recovery of the phosphate from this source. These deposits, located at Bu-Craa 100 km from the Atlantic coast in the northern part, was discovered in May 1963. The thickness of the mineral layer yellowish light brown varies from 2.5 to 7 metres, which breaks easily. Based on beneficiation trials carried out on a semi-industrial scale, two grades, viz. 75 and 85 per cent concentrate, have been commercialized by Fosfatos de Bu-Craa. Plants have been built for the first stage production of 3,000,000 tes of concentrated rock, while for a second stage production per year of 6,000,000 tes units are under construction.

The development of the deposit begins with the mine; the mineral is mined by a stripping method evolved after a considerable study of the existing experiences and through a pilot plant study. The material is loaded into 100 te bottom trucks carrying the mineral to the feed hopper of the crushing plant at the mine. The grain of less than 10 mm. diameter to the first intermediate stockpile at the mine and to the second intermediate stockpile at the coast after travelling 100 km through desert. From the second intermediate stockpile the materials rolls into the beneficiation plant where a wet process using sea water is used for beneficiation. The concentrated materials is loaded from storage points into vessels at 4000 tes/hr which can be performed in 3 berths situated at the end of a 3,200 metre long pier.

A power plant with a capacity of 56 MW to be raised to 96 MW in the third stage has been built to supply power to the overall complex and to bring fresh water to the beneficiation plant.

The mines would produce 1 million tonnes of rock during 1973 the start-up year—and 3 million tonnes during 1974. The company envisages production of 5 million tonnes in 1975, 6 million tonnes in 1976, 8 million tonnes in 1977 and 10 million tonnes during 1978-79 and onwards. The Bu-Craa reserves are expected to last for 100 years.

During the 10 year period ending 1971-72, world fertilizer production and consumption have more than doubled reaching 76.7 and 73.6 mil. tonnes respectively, and owing to expanding population and

the current world situation of limited supplies and rising prices, consumption of fertilizers is expected to increase at the present high level. The rates of growth in the case of developing countries have been greater than in the case of developed countries—they will reach 20 mil. tonnes in 1976-77 and 30 mil. tonnes in 1979-80 representing a doubling of consumption in 5 years and tripling in 8 years. Most of the developing countries will continue to depend heavily on imports. According to S. Krishnaswami⁸, in the present situation of fertilizer shortage in the international markets the developing countries should seek to get their share by long-term contracts. The export prices should be remunerative, providing for reasonable profit, after providing for the large increase in production costs, high freight rates and heavy investment in pollutions control. In this connexion he mentioned the Government of India's long term understanding with Canpotex (Canada) on the supply of potash.

Japan is one of the leading producers and exporters of nitrogenous fertilizers in the world. To overcome the nation's food shortage after the devastation of the Second World War, the Japanese fertilizer industry was promptly rebuilt. According to S. Hayashi⁹ of the Japan Urea and Ammonium Sulphate Industry Association, the ammonia and nitrogenous fertilizer industry developed as the main part of chemical industry. During the past few years the production capacity of ammonia has doubled and that of urea trebled. Ammonium sulphate and chloride are losing ground in favour of urea and high analysis fertilizer. Consequent on changes in the Government's agricultural policy, the fertilizer consumption started rising after 1970. Due of excess production, the inventories rose to the level of 5 months production in 1972, resulting in lowering of export prices. However, at present this situation has changed with increase in domestic consumption and in overseas demand; the excess inventories have disappeared.

The resources depletion and the environmental pollution problems are bringing about a shortage of raw materials and a critical situation in energy and restraints on production activities. Neither any increase in the existing ammonia and urea production capacities nor any new capacities are envisaged.

⁷. The Prospects of Availability of Phosphate Rock from the Spanish Sahara.

8. World Fertilizer Situation in the Seventies : Japanese and American Scene by S. Krishnaswami, Jt. Secretary, Union Ministry of Finance, New Delhi.

9. The Present Status and Prospect of the Japanese Nitrogenous Industry by S. Hayashi.

Though output of ammonium sulphate may rise but its export availability will not. It will be the same as in the previous year. Some decrease in urea availability is predicted. It is believed that Japanese exports of nitrogenous fertilizers touched the peak last year and will decline. The large increase in production costs, high freight rates and heavy investment in pollution control demand that export prices should be remunerative so as to cover costs plus reasonable profits.

The world's population of 3.7 billion people depend upon the farmer for food, but according to William C. White¹⁰ the grain consumption in 1974 will exceed grain production; in USA such a shortage is a new experience and the four feed grain stocks on October 1, 1972 consisted of 41 mil. tes down to 26% from Oct. 1972, the lowest in the USA since 1952. The American farmers are in great need of fertilizers with the common place use of the 1 to 10 ratio of plant nutrients and grain production. The net farm income in 1973 is estimated to be about \$24 billion compared with about \$19 billion in 1972, the difference being the increase in prices received by the farmers. With greatly improved profits, the American farmer will be a high bidder for fertilizers. Two devaluations of the U.S. dollar have added to the attractiveness of US fertilizer export. This condition together with increasing domestic demand have brought fertilizer shortages in 1973. The decontrol of fertilizer prices will tend to divert export supplies to meet domestic demand.

The shortages will be most severe in nitrogen, amounting about 1 million short ton of nitrogen, but less severe in phosphate, say about 400,000 short tons of P_2O_5 . Moreover, inadequate transportation and production cut-backs resulting from energy shortages and environmental regulations. Energy shortages are disabling ammonia production which is based exclusively on natural gas, whose supply is being curtailed. However, coal-based feedstocks for ammonia production will not be economically feasible at least for another 10 years. About phosphate situation profit margin is not only low but beset with energy problems and with the serious obstacles of environmental controls and restrictions on land and water use phosphate industry's expansion will be gradual in the next several years. The assessment of the American fertilizer scene underscores the urgency of nations

selling and buying fertilizers working cooperatively together; they must determine as far ahead as possible each other's supplies and needs and arrange contracts that provide as much as dependability and constancy as possible in international fertilizer trade.

The world potash production has reached almost 20 million tonnes K_2O_5 in 1972-73 and is expected to grow to 30 million tonnes in 1980. Under today's short supply situation, buyers of fertilizer materials are primarily concerned with assuring themselves with a quality product with dependability of supply and a fair price. In an informative paper¹¹, R.E. Hatch presented the present situation of the world potash industry with special reference to Canada. Canadian potash industry is the only source with reserve production capacity, which is sufficient to meet the world's needs for a long time. U.S. and Canada supply 96% of N. American demand. The European Producer Group supplies 78% of the needs of the W. Europe and E. Germany and USSR supply 99% of the needs of COMECON. However, with U.S. supplies diminishing, Canada has become an increasingly important supplier to markets in Asia, Oceania and Latin America. CANPOTEX is a Canadian commercial organization owned by private potash mine owners; its aim is to significantly and quickly increase Canada's export of potash. It will be the major supplier to India. The long-term understanding between the Indian Government and CANPOTEX will ensure adequate potash supplies for India.

Production of Ammonia From Heavy Fractions as Feedstock

Inaugurated by Sri Shah Nawaz Khan, Union Minister of State in the Ministry of Petroleum and Chemicals, Govt. of India, the keynote address¹² of the second day's seminar was delivered by P. K. Dave, Secretary, Ministry of Petroleum and Chemicals. Analysing briefly the different feedstocks for ammonia in India, he stated that while the availability of natural gas is limited, our experience with coke oven gas from steel plants has not been too happy because of its uncertain availability. In the same way, the electrolytic process is not an acceptable proposition, because of more compelling demand for

10. The American Fertilizer Science for 1974 by W. C. White, The Fertilizer Institute, Washington, D.C.

11. The World Potash Situation in the Seventies by R. H. Hatch, Canpotex Ltd., Toronto.

12. Technical and Economics Aspects of Ammonia Production by P. K. Dave.

power for socially more important use. Similarly, refinery gas can only be used as a supplementary feedstock and lignite which has played only a limited part is unlikely to be used in increasing amounts in the fertilizer industry in India. During 1960s when we had a surplus of naphtha from our refineries the planning of fertilizer production was based mainly on this fraction but with the development of petrochemicals industry for which naphtha is the main raw material, further growth of fertilizer industry based on this feedstock was not considered feasible. In the latter half of 1960s the Feedstock Committee considered the import of liquefied natural gas liquid ammonia, naphtha, crude oil and heavy fractions of petroleum. While this committee considered the possibility of using coal as a feedstock and approved the construction of the 3 coal-based projects, its recommendation heavily weighed in favour of the heavier fractions of petroleum. It even preferred the import of these fractions over that of the more expensive naphtha and therefore the fractions were exempted from excise duty when used for fertilizer manufacture. The 8 or 9 fertilizer plants programmed for construction during the Fifth Plan in addition to the 3 plants already in various stages of construction and another already planned are all based on fuel oil or crude. Sri Dave suggested the distinguished gathering to consider the possibility of switching over the use of naphtha in the primary reformer to fuel oil or other fuels in the light of the present developments in the material of construction.

With the developing world oil situation, the possibilities of further fertilizer plants are going to be based on coal. It has decided that any captive power generation and the above mentioned fuel oil based fertilizer plants will use coal for steam generation.

The shortage of naphtha and the recent trends in the relative prices of naphtha and heavier petroleum and their availability have created interest in the partial oxidation route¹³ for ammonia production using heavy petroleum feedstocks. Prior to development of the reformation catalyst for processing naphtha or light petroleum fractions partial oxidation was the only route developed as early as 1952-54. Of the several processes, Texaco route has over 60 plants with a total output of over 1 mil. standard cubic feet per day of synthesis gas, while

the Shell gasification route has a total output of over 1.2 mil. standard cubic feet world over, both being noncatalytic processes using oxygen for partial oxidation. The four plants in India, viz. at Trombay, Gorakhpur, Ennore and Alwaye, are based on the Shell process though processing naphtha. Both the routes have tended to adopt all the more important and salient features minimizing thereby significant differences between the two processes. As developed originally, the Shell process adopted a waste heat boiler after the gasifier for recovery of the process heat; the carbon in the process gas was recovered as a slurry in water and pelletized with fuel oil and used as fuel in boilers for steam generation. The Texaco process adopted direct quench for cooling the process gases; the carbon was recovered and recycled as a slurry in the feedstock thus minimizing problems in the disposal of the recovered carbon.

The author has critically analysed the gasifier size and pressure waste heat recovery, carbon recovery, recycle and stream efficiency of both the routes giving the instances of two large plants, viz. BASF at Ludwigschafen (Texaco process) and VEBA Chemie (Shell process) at Gelsenkirchen. The experiences of the above two large plants are reassuring but the industry, accustomed in recent years to extensive reliance on natural gas and naphtha as the preferred feedstocks, still has some hesitation in accepting the partial oxidation process though not always for some technical reasons.

Most of the synthesis gas and hydrogen is produced now-a-days from oil products, the major part derived from natural gas, refinery gas and naphtha by the catalytic steam reformation process but since 1955 heavy residual oil products have gained in importance owing to the versatile partial oxidation process. World-wide installed production capacity of oil partial oxidation units currently amounts to some 77,000,000 Nm³/sd of synthesis gas, which represent about 10% of the syn gas requirements. L. W. Ter Haar and F. K. G. Ouwerschuur¹⁴ have dealt with the experience obtained with the Shell gasification process, which is being used in 19 countries for the manufacture of synthesis gas for ammonia, methanol and oxo-alcohol synthesis and also for town gas and reducing gas in some countries.

13. Prospects and Problems of Partial Oxidation Processes by S. Venkataraman.

14. Developments in Synthesis Gas Production by Partial Oxidation of Heavy Fuels by L. W. Ter Haar and F. K. G. Ouwerschuur, Shell International Petroleum, The Hague, Holland.

Any hydrocarbon can be partially combusted with oxygen or air according to



the reaction temperature approaching that of a normal flame which obviates the use of a catalyst. The fuel consumption is about 4 tons/ton of H_2 increasing to about 4.6 ton including CO conversion and methanation steps. Some steam is used as a moderator, primarily to control the reaction temperature and owing to the relatively high reaction temperature, the methane content of the product gas is low (less than 0.6% vol.) even at 50-60 atm. Due to low steam dosage, little CO-shift takes place in the reactor and for NH_3 and methanol synthesis and hydrogen manufacture tailor made syn gas is produced by controlled CO-shift in a subsequent process unit. The majority of the partial oxidation units are processing heavy oil products. The Shell process produces 100 atm. abs. saturated steam in a waste heat boiler. After super-heating, the major part of the steam is let down in a back-pressure turbine to process it for CO-shift and L.P. steam for desulphurization, which is generally sufficient to compress the product to 150 atm. abs. Since oxygen compression above 70 atm. in centrifugal compressors has not yet been proven and the specific equipment cost of the total train also increases above the 60 atm. abs. pressure level, the train which delivers gas at 55 atm. abs. and produces 100 atm. abs. saturated steam in a waste heat boiler is preferred.

The capital investment in a steam-reforming process is some 85-100% of the partial oxidation train if the oxygen plant is excluded. The total consumptions of feed and fuel are roughly equal for all both trains. At an equal product cost the break-even price differential between the steam-reforming feedstock/fuel and the partial oxidation feedstock will be largely determined by the oxygen price. The development of large scale plants will, therefore, favour the partial oxidation route; the cost of power for the oxygen plant (steam drive in large units, electric drive in smaller ones) also appears an economic factor of importance. For a 1200 t/d ammonia plant about 1000 t/d of oxygen will be required which on that scale will cost \$12./ton. Since for partial oxidation about 1 ton of oxygen per ton of residual oil is required, the break-even price differential with naphtha at this scale of operation will also amount to some \$12./ton.

The flexibility of utilizing by-product steam for any desired purpose has given considerable credit to par-

tial oxidation units equipped with waste heat boilers. Since its commercial introduction in early fifties, the following developments in partial oxidation route have been of importance: (i) reduction of gas compression cost by increasing the process pressure from 20 to 60-85 atm. (representing a saving of 100 kWh/ton of NH_3); (ii) increase of reactor production capacity from the equivalent of 50 to 455 t/d of NH_3 , thus representing a reduction in capital investment by about 50%; (iii) improvements in the disposal of by-product carbon; (iv) improvements in waste-heat recovery.

In the reactor, the oil feed is subjected to partial combustion with 35% of the stoichiometric oxygen requirement, some steam being used to moderate the flame temperature. The gas needs to be cooled down below its dew point to ensure efficient carbon removal. The waste heat boiler used in the Shell process has the following advantages: (i) high pressure steam can be raised for both power recovery and process use, (ii) conditions for optimum carbon removal can be selected independently of these of heat recovery. Carbon is removed in a 2-stage water wash operating at low temperature (40-150°C) upto less than 1 ppm. The carbon water slurry contains 1. 1.5% wt carbon (amounting to 2-3% wt. on feedstock) from which carbon is agglomerated with oil and separated by a pelletizing separator.

Today more than 100 reactor waste heat boiler units are licensed to industry processing mostly residual oil. Sulphur in the feed is easily removed by the sulfinol treating process, which renders the gas suitable for the use of the modern 1.t CO-shift catalyst. Shell gasification units have excellent maintenance record. Among the recent developments of the Shell process, the following are notable: (i) a versatile carbon recovery process particularly suitable for processing feedstocks heavier than propane asphalt and vacuum pitch; (ii) design of large size units capable for producing syn gas equivalent to 455 t/d NH_3 ; (iii) design of waste heat boilers for high steam pressure.

Till now only 20% of the ammonia production is based on partial oxidation because of the low price differential between naphtha and fuel oil (Bunker C) existing before 1972. At the differential prices of \$12-\$17 prevailing till August 1973, partial oxidation becomes more attractive than steam-reforming—in fact at reduced unit size the price differential increases.

In the next paper¹⁵, E. T. Child and C. P. Marion gave the recent developments in the Texaco synthesis gas generation process. Strong awareness of air and water conservation problems and increasing demands for energy have eliminated the surpluses of natural gas, naphtha and distillate petroleum fractions, which has led to an increasing interest in high-sulphur residual oil fractions and coal as logical feedstocks for ammonia production. Texaco have placed emphasis in developing highly reliable and flexible process that will work on a variety of feedstocks over a wide range of pressures and in virtually any size of plant. Their study have also included the optimum integration of the process into a refinery as well as possibility of operating the gas-generation and purification plant at a high enough pressure that it matches the inlet pressure to the ammonia plant. Much of this development work on the manufacture of hydrogen has been carried out at Montebello Research Laboratory near Los Angeles, where a large scale high-pressure, single-train pilot plant is available for research and development. Their commercial generators operate in two modes ; one is with direct water quench where high pressure steam is produced directly in the syn gas stream, most of the soot is removed in the lower section of the generator and the gases become saturated with water vapour so that no additional steam is required for shift conversion. In the waste heat boiler mode, high pressure steam can be recovered by cooling the hot syn gas but steam has to be added back to the gas stream entering the shift converter. The first type is often favoured in ammonia or hydrogen plants in which steam is required for the shift reaction. A number of different size generators are available in standard design which have been operated up to 85 atm. on a commercial scale. The large scale pilot plant studies have indicated that there are no technical obstacles to designing and operating generators at pressure upto 170 atm. and single generators are capable of producing more than 3 million Nm³/day of hydrogen plus carbon monoxide, equivalent to about 1400 tes/day of ammonia.

The 1-3% of the feedstock that is converted to soot (on a single-pass basis) when operating with heavier feedstock is almost entirely removed from the gas in the water-quench chamber with the final traces being removed in a scrubbing nozzle.

A wide variety of sulphur-containing distillates and

residual fuel have been used commercially and the recent trend is very viscous materials. The authors described 3 shift-conversion catalysts of which the most active commercially-available one contains copper and zinc, but BASF has developed a superior catalyst (cobalt molybdenum) which requires sulphur to get activated. In this connexion they mentioned the studies carried out by Texaco using coal-oil or coal-water slurry for use as a feedstock towards which a successful commercial-scale demonstration has been successfully completed using 87 metric ton/day. According to them, substantial savings can be achieved by effective integrations of an ammonia plant into a refinery having the following advantages: (i) the naphtha-soot stream can be sent back to the atmospheric distillation tower for recovery of naphtha, (ii) the gasifier can use virtually any hydrocarbon stream in a refinery as charge stock so that balancing of the refinery is simplified and vacuum-tower bottoms are used as feedstock (iii) a single synthesis gas generations unit can produce hydrogen suitable for both hydrotreating and ammonia synthesis, (iv) a single Claus unit can process the H₂S streams from both the refinery and synthesis gas units, etc. They gave an idea about the potential for balancing a refinery by considering the case of a 1000 te/day ammonia plant unit 750 te/day of high sulphur vacuum tower bottom integrated into a refinery.

Considering self-reliance as the most important criteria, coal-based ammonia plants would be the natural choice for our country but they have the following limitations: (i) long maturation time in developing the coalfields; (ii) technology has still to be proven on a scales larger than 900 t/d ammonia; (iii) a very much higher capital on equipment and consequently a much high cost of ammonia.

At present, about 3 mil. tes of fuel oil is produced in India all of which is used as industrial fuel. Some of it is also imported. With the expansion of the refining capacity to around 36 mil. tes by 1979 there might be an additional production of 1.5 mil. tes. The entire quantity will be just sufficient to meet the requirements of fuel oil-based ammonia plants which have already been planned, according to J. P. Kapur¹⁶. Till such time we expand our refining capacity further, fuel oil can be made available. In evaluating the economics of setting up ammonia plants (1000-2000 te/d of NH₃) based on fuel oil, the author has consi-

15. Recent Developments in the Texaco Synthesis Gas Generation Process. E. T. Child and C. P. Marion, Texaco Development Corporation, USA.

16. Fuel-Oil-Based Ammonia Plants by J. P. Kapur, DCM Chemical Works, New Delhi.

dered the following points: (i) production cost at various feedstock prices (ii) capital cost escalation; (iii) impact of scale of operation and (iv) foreign exchange outflow for import of plant and feedstock.

On the basis of base prices of Rs. 180/te of imported fuel oil and Rs. 40/te of coal and an escalation of 25% rise in fuel oil price and 10% for coal price, fuel oil-based plants would produce cheaper ammonia for about 5 years from now. According to the author the scales of operation feasible in the next 5 years, limited by technology are 1000 t/d. NH_3 for coal-based plants and 1500-2000 t/d for the fuel oil-based ones. This gives the larger fuel oil-based units a marked cost advantage over the coal-based ones. Another advantage for the large fuel oil-plants is the impact of capital cost escalation, which is about Rs. 120/te for NH_3 over the coal-based units.

The major advantage of a fuel oil-based technology is that it can take a wide range of feedstocks without capacity being affected while the major drawback is in the handling and recovery of carbon. Fairly large plants (upto 2000 te/day NH_3) are technoeconomically feasible. However, the author admits that in the long-term planning in India coal is the only feedstock and, therefore, suggests that in the planning of the new large fuel oil-based plants, the possibility of converting them to coal-based units should be in-built in the design equipment and layout. The location of the 4 new 1500 t/d NH_3 plants based on imported fuel oil to be set up by 1979 should preferably be located at ports and in the meanwhile coalfields should be identified and transport network established so that the above fuel-based plants be switched over completely or partially to coal in fact, the use of coal in Texaco process offered considerable scope for gradual replacement of fuel oil with coal.

Fuel oils are becoming more attractive as feedstocks in the petrochemical industry because of the pollution problems in burning them on account of their sulphur content and of the sky-high prices of the lighter fractions. In this context, the partial oxidation process is gaining interest for the production of NH_3 . The Texaco partial oxidation process¹⁷ operating at 80 atm. results in considerable compression horse power savings and improved heat recovery. This saving in horse power is easily demonstrated when considering that one volume of oxygen produces about 3.8 volume of hydrogen although a small fraction of

this is lost by pumping to a higher pressure the water for carbon removal and the solution for CO_2 and H_2S removal. Another advantage of the higher pressure operation is the possibility of condensing an appreciable fraction of the CO_2 contained in the raw, gas during the CO_2 removal stage, thus obtaining pure liquid CO_2 which is pumped to the higher pressure required for the synthesis of urea. This feature has the advantages, like saving of the CO_2 compressor with all the associated downtime risks, horse power saving and availability of aspare machine for liquid CO_2 pumping at a little extra cost. Two large commercial plants with a Texaco gas generator at this pressure level have been operating satisfactorily and with an on-stream factor as good as that usually achieved on conventional steam-reforming plants. With the new BASF shift catalyst (cobalt and molybdenum oxides) having a strong refractory carrier and a high shift activity in the range 300-350°C, it is now possible to perform the shift conversion directly after the Texaco gas generation without prior sulphur removal (even if the feedstock contains 6-7% sulphur). This new catalyst has been in continuous operation at Ludwigschafen under 80 atm. pressure with very satisfactory results. Another process simplification is the use of liquid oxygen pump to boost the oxygen to the pressure required for the partial oxidation reaction. A fraction of the oil feedstock is used to recover the carbon produced in the gas generator and recycle it in the form of a slurry to the generator inlet after mixing with the main oil stream giving the highest yield with respect to the oil feedstock and eliminating any problem of carbon disposal. A central boiler produces high pressure (above 100 atm.) steam for driving centrifugal machines and supplying the process and heat requirements of the plant and having one or two of the large steam turbines using this steam with partial extraction at an intermediate pressure.

The various problems faced in operating EID—Parry's Shell gasification plant from 1952 at Ennore (near Madras) have been described by K. V. Ratnam and E. S. Murthy¹⁸. This factory is designed to produce 158 tes of ammonium sulphate phosphate (16:20:0) and 110 tes of ammonium sulphate per day. Till now its reactor, working at 30 kg./cm.² and 1350-1400°C, had to be relined frequently due to deterioration of the refractory at the nose portion. This problem was overcome with the introduction of a mono-

17. Production of Ammonia by Texaco Process by D. Banquy, Soc. of Foster Wheeler Francaise, Paris.

18. EID—Parry's Experience in Naphtha Gasification by K. V. Ratnam and E. S. Murthy.

lithic refractory ring which can be replaced from the top without disturbing the brickwork in the head. A special feature of this ring was that it was easily replacable from the top, i.e. from the nose. In case of deterioration, the ring could be easily replaced without the necessity of removing the head, whereas earlier the whole head used to be brought down and the entire brick/work redone. Subsequent to a mishap in 1963 involving failure of the atomizer gun, they put a limit of 3,000 hours for using a gun even if it was in a good condition. The authors underscored the need for obtaining technical know-how to carry out repair of guns locally instead of sending abroad the used ones for repair. The paper also dealt with the problems of carbon recovery and disposal—one way of utilizing the carbon was to make activated carbon from it.

In the next paper¹⁹, the author T.G.C. Pillai gave the experiences of the FACT of their two partial oxidation plants using naphtha in the Texaco process, which were commissioned in 1962 and 1966 respectively. The first plant is of 80 tpd. capacity while the second 140 tpd. One of the important causes for a large number of shut-downs of the plant was frequent power failure: 56% of the shut-downs were either directly due to power failure or the result of power interruptions, 12% due to instrumentation failure and the remaining 32% due to reasons, like lack of demand, scheduled shut-downs, shut-down for boiler inspections and operational difficulties. Among the problems encountered in the early stages was frequent breakdowns of the oxygen compressors due to damage to valve-discs, springs, valves, valve chair, skirts, etc. With the commissioning of the tonnage oxygen plant in 1965, the oxygen compression lost its importance as the main source of oxygen supply. Carbon removal posed its own problem but this was overcome by installing Venturi scrubber between the generator and the scrubber for wetting the carbon before removal, which brought down carbon in the gas to less than 1 mg./cu.m. Erosion of pumps made of cast steel was another problem which was overcome by using stainless steel. The paper analysed the causes of fire and explosion hazards in the different sections and particularly naphtha fires and outlined the steps taken to prevent recurrence of such accidents. The performance of all equipments, particularly preheaters generators and accessories is given. The

conversion and water wash section have also been touched briefly.

In the FCI's Trombay plant there are 4 shell reactors for the production of 350 M.T./day of NH_3 laid out of 2 reactors in parallel in each train using naphtha/refinery gas as feedstock using non-catalytic Shell gasification process. The reactors operate 31 kg./cm.² pressure and 1,400°C. During the start-up in Nov. 1965, it was found that the specific gravity of the gas (from a nearby refinery) was very low and the supply fluctuating widely, causing serious accidents and fire. So the use of refinery gas was discontinued. Their experience with fuel oil was also not satisfactory since it resulted in frequent clogging of guns thus causing shut-down of gasifiers. Frequent tripout of feedstock pre-heater burners due to carry-over of condensate along with refinery gas used as heating medium was also experienced. Besides this, malfunctioning of burner control valve also contributed to trip out. An additional catch pot was installed on the main refinery gas line and the refinery gas line to the feedstock preheater was steam traced to avoid condensation accumulations which improved the performance.

The authors²⁰ presented a critical analysis of functioning of the reactor, waste heat boiler and the carbon scrubber section. In the reactor section, annual inspection of the brick-lining for cracks, looseness of bricks, wear and tear was done as a routine. Shrinkage of bricks was noticed in a 9 inch liner in a period of 3 years' operation. The average life of a brick was of the order of 8,000 hours. Malfunctioning of tripout switches provided for safety shut-down systems caused frequent tripping of the reactors; the switches were, therefore, replaced by pneumatic transmitter.

The 6 years' performance of the FCI's Shell gasification plant at Gorakhpur using naphtha was good, having the minimum down-time and 98% stream efficiency. Analysing the operational experience, A. S. Chatha and A. C. Dora²¹ made the following recommendations for trouble-free operation: (i) cleaning of naphtha bulk storage tanks and day tanks every year; (ii) steam and nitrogen flushing of naphtha preheating lines at regular intervals; (iii) acid washing followed by water washing of waste heat boilers and combustor nose at regular intervals; (iv) regular cleaning of quench filters, quench cooler tubes, carbon scrubber

19. Operating Experience of FACT of Partial Oxidation Plants by T. G. C. Pillai, FACT Udyogamandal, Alwaye (Kerala).

20. Trombay's Experience of Shell Gasification by Y. R. Pakkala and K. Govindrajana, FCI, Ltd., Trombay.

21. Operating Experience of Shell Gasification Plant at Gorakhpur by A. C. Chatha and A. C. Dora.

cooler tubes and slurry lines; (v) annual inspection and cleaning of carbon scrubber distributors and packing; (vi) annual inspection of reactor refractory; (vii) ultrasonic testing for determining erosion rate; (viii) change of the design of the quench coolers so that they can be washed effectively; (ix) increase quench nozzle capacity to feed 10% extra water for quenching to reduce the temperature of gas outlet as well as carbon content in the gas outlet slurry separator, particularly when the plant is running with carbon scrubber cooler by passed.

According to I. M. Skotgested²² of Norsk Hydro, Norway, ammonia plants based on partial oxidation are about 30 per cent more expensive than the corresponding plants based on steam-reforming, the fuel requirements being also normally higher. On the other hand, maintenance costs are somewhat lower and the on-stream factor is 2-3% higher than a steam reforming plant. Their heavy fuel based 600 tpd. plant at Heroya started in 1965 with an annual design capacity of 120,000 t of NH_3 and 50,000 t of methanol. Their present capacity is 190,000 t of equivalent NH_3 . The plant comprises the following: (i) three type 500 Shell reactors (2 operating and one spare) having gasification pressure 35 bar; (ii) for removing sulphur compounds down to 20 ppm. Shell sulfinol process; (iii) the sulphur compounds in the off-gases are treated in a Claus plant for production of elemental sulphur with the resulting total sulphur emission to the atmosphere in the order of 1 tpd SO_2 ; (iv) high temperature CO-shift conversion with cooling saturation cycle; (v) high efficiency water wash for removal of CO_2 down to a level of 300 ppm CO_2 in the exit gas; (vi) NaOH wash for trace removal of CO_2 ; (vii) liquid N_2 wash which gives a very pure synthesis gas often obviating the necessity of purging in the ammonia loop; (viii) ammonia synthesis and (ix) methanol synthesis.

The plant is at present run continuously with 2 reactors changing the reactor every fourth month, the maximum load being 240 tpd. of fuel oil giving plant stream efficiency of 93.7%. They have found evolutionary operation (EVOP) techniques (simplex version), extremely useful in finding the optimum conditions; oxygen/fuel and steam/fuel ratios are systematically changed to optimize the gas yield. They have found pre-reduced ammonia synthesis catalyst more acceptable for its short initial start-up

time (24 hours against 6 days for the conventional catalyst).

H. Badura and H. Butzert²³ of Veba Chemie with M. Brejc and E. Supp of Lurgi have outlined the design philosophy and operational experience of Veba's new 1,200 mtpd ammonia-cum-600 mtpd methanol plant incorporating four Shell series 1,000 gasifiers using Visbreaker vacuum residue (from its refinery within the complex) as the feedstock. The complex comprises air separation, Shell gasification, Rectisol H_2S removal, h.t. CO shift conversion, Rectisol CO_2 removal, liquid nitrogen scrubbing, ammonia synthesis, refrigeration unit, cold tank farm, methanol synthesis and distillation. They have found 60 kg./cm.² gasification pressure optimum as the drives of the turbocompressors require a total of about 80 MW of power; 80 kg./cm.² abs. steam from the waste heat boiler drives the synthesis gas and refrigeration turbo compressors, the high temperature CO shift conversion and Shell gasification. The rest of the energy is required for the electric drives of the two air turbocompressors, the oxygen and nitrogen turbocompressor. Sulphur-free tail gases from Rectisol and nitrogen scrubbing were used for superheating the 200 t/h steam from the overall plant. Shift conversion was designed for a sufficiently high residual CO content in order to obtain enough heating value from the nitrogen scrubbing tail gas. Only Shell gasification has 4 trains, while air separation, Rectisol wash, CO shift conversion, nitrogen scrubbing and NH_3 synthesis have one train.

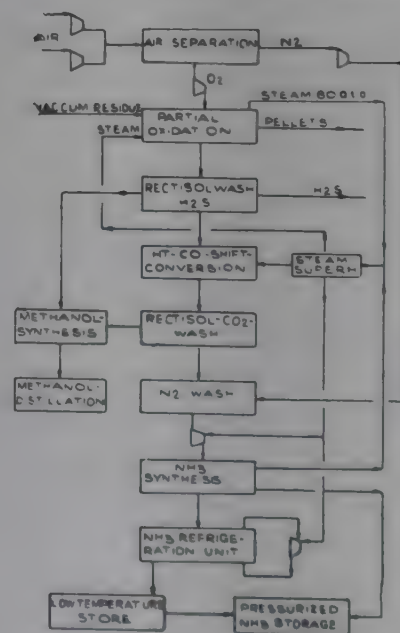


Fig 1—Design Features of Veba Ammonia Plant

Fig 1—Design Features of Veba Ammonia Plant

22. Some Experience in the Production of Ammonia from Heavy Fuel Oil Feedstocks by I. M. Skogestad.

23. Veba Ammonia Plant Based on Partial Oxidation of Heavy Feedstock.

Regarding infrastructure of Veba works, there is a connexion to an oxygen system for import and export, high pressure steam and electric power are supplied from a nearby power plant where pellets from Shell gasification are fired, H_2S from Rectisol wash is converted, to elemental sulphur in a Claus kiln, ammonia synthesis gas can be sent to other ammonia plants of Veba, and ammonia is transported by pipeline or tank trucks to other Veba plants for further processing.

The authors have discussed the problems arising from the incorporation of all the new units into the complex and recommended to have the engineering of the entire plant in the hands of one engineering firm. They also emphasized the importance of proper training of the operating personnel.

Kenura Oy, the only manufacturer of fertilizer in Finland, started ammonia production at their Oulu works in 1952 from coal using Koppers-Totzek process. Since 1956 heavy fuel oil has been used as feedstock. The start-up of the first Shell pressure gasification unit with soot pelletizing took place in 1965 and the second Shell unit was started in 1973, when

the homogenization of the soot to fuel oil as well as its recycle back to gasification were introduced. P. K. Knuttila of Kemira Oy Finland presented a summary of his company's experience with partial carbon recycle gained over the last 6 months in the two Shell pressure gasification units. This experience seemed to indicate that carbon recycle to the extent of two-thirds of the total had no significant effect on the economy of plant operation—a 3-4% increase in oxygen consumption being nullified by a small decrease in feedstock consumption.

Until 1973 carbon was pelletized and used as an additional fuel with coal in the boilers but with the changeover of the boilers to oil-firing homogenization of soot pellets into fuel oil and the utilization of this soot-oil mixture as a raw material in the gasification plant as well as fuel in the boilers are being carried out. The part of the carbon, which was burnt with fuel oil in auxiliary boilers, caused increased corrosion and slag formation in the boilers. On the other hand, a total recycle was regarded as a risky solution because of high ash concentration in the recycle and eventually faster wear of reactor lining.

Library and Documentation Systems

Libraries and library services (including documentation services) have come to be recognized as an essential part of modern education, research and industrial development. The nature of a library and its services are obviously in tune with the objectives of the library's parent organization. The professionals from different educational, research and industrial organizations have, therefore, their own peculiarities of approach to the common objectives and problems of libraries, namely, information retrieval.

To pool the experiences in different libraries by their respective librarians, the Documentation Research and Training Centre (DRTC), Bangalore, organized its 11th Annual Seminar on Planning of Library and Documentation Systems at Bangalore during February 10-15, 1974. The seminar was attended by documentalists, librarians and university teachers from various parts of the country. There were about 20 papers on such diverse library topics as systems approach to communication of information, cost-benefit analysis of library and documentation services, use of computers in library services, planning of national information systems in general, as well as for speci-

fic subjects, like fisheries, planning and execution of need-based information retrieval systems, etc. Some of the papers presented case studies also.

The professional gathering has taken it for granted that planned libraries exist in all organizations and what is required is only planning (and implementation) of library and documentation services. Having started from this assumption, the first paper presented at this seminar gives an exhaustive idea of 'what,' 'why' and 'how' of a national information system. Systems approach is the main feature in this paper and a set of features and factors to be considered in developing a plan for national information system was presented. The authors contend that several techniques developed in other fields such as program budgeting, flow charts, PERT, CPM and simulation techniques provide useful guide in the methodology for planning library information systems and therefore advocate that advanced courses in library and information services should lay emphasis on teaching library and information systems as a discipline.

Elaborate plans for rendering library and documentation services were given by the librarians of Central

Machine Tools Institute, Bangalore, Central Leather Research Institute, Madras, Central Food Technological Research Institute, Mysore and Central Marine Fisheries Research Institute, Cochin in their respective subject fields.

That there should be a need for a national information system in a particular field of knowledge is amply established by A. Rahman in his paper by stating that 'The impetus and immediate trigger in formulating a plan for National Information Centre for machine tools has been provided by the *Emergency Plan for self-reliance in machine tools technology* by the National Committee on Science and Technology (NCST) (page 192)'. A consequence of this statement of NCST is the establishment of a National Information Centre for Machine Tools for which plan has been drawn with well-defined objectives and functions. The plan includes every aspect of communication of knowledge from the place of its origin to the last step when it reaches the user.

Apart from the proposed plans for library and documentation services at national level on specific subjects, plans were also given for such services at local levels. In this context, the areas of co-operation among the organizations at national and local levels were identified in the paper by P. Jayaraman.

The cost of local abstracting periodicals and cost-benefit analysis of library and documentation systems are the topics of one paper. In yet another paper on the same subject, the author went a step ahead and stated that cost-benefit should be the prime factor for initiation of any library (and documentation) services.

Assessment of users' needs periodically is one most important factor on which stress has been laid in order to see that perfect matching is possible between a reader and his information needs. Planning of this matching of specific information with its potential user—Selective Dissemination of Information (SDI)—requires strict implementation of the plan, if it is to be a success. How this should be done has been described with case study in one article, the case study being that of the National Aeronautical Laboratory, Bangalore.

The need for a cell for developmental research in documentation in every library has been stressed in one paper. It was also advocated that the librarian working in a particular subject library should develop his own depth subject schedule.

Though the subjects of various special libraries are different, e.g. chemical technology, electronics, agriculture, etc., the methodology of technical processing of documents and rendering of library and documentation services in all libraries will be, more or less, the same. In this context, there is ample scope for standardization of procedures and processes in the library and documentation services. The author on this subject feels that library standards should be formulated based on the experiences gained and the standards, thus evolved, should be followed in the larger interests of the profession. It was also proposed that the new entrants should be taught to follow the library standards. The author also gave comparative data on the subject from UK and USA.

There are Indian, British as well as international standards in the field of library science. Variations, however, exist among these standards. A particular information tabulated according to Indian Standards, for example, requires modifications when the same is required to be presented at international level. One problem that comes under this category is the abbreviated titles of Indian periodicals. In the Bhabha Atomic Research Centre, Bombay, this problem was sought to be solved by means of computer and accordingly COBOL programme for H-400 system was developed. The titles of 900 Indian periodicals were thus abbreviated and standardized. It has been claimed that list of titles of Indian periodicals with standardized abbreviated titles can be circulated even to other institutions.

The professors at the DRTC have prepared draft plans for library and documentation services in Hindustan Aeronautics Ltd., Bangalore, Tamil Nadu's Department of Industries, Guindy, Oil and Natural Gas Commission, Dehradun, Central Food Technological Research Institute, Mysore, etc. Based upon the experience, thus gained by them, they had given draft plans for Central and Regional units of library and documentation services.

A small number of other articles give an idea of the nature of their libraries and peculiarities of the services now being rendered by them with statements of objectives and functions.

The last* of the papers incidentally happened to be by this reviewer. The point highlighted in this paper was of basic nature: To what extent the libraries

* Planning of Libraries and Library Services in India
by C. Y. Rao

are well-planned, to think (and then act, if possible) of plans for its services? At least one instance where there are no planned libraries in a national level research organization was cited. It was also recalled how a well-thought of plan prepared by professionals of a very high standard was watered down when it came to be implemented. This point was, however, cited to highlight the need not only for just planning, but to emphasize the need to see that the well-intentioned plans are properly implemented with professional interest.

It is fundamental that every library should have well-defined objectives and functions. These should be followed by appropriate technical manpower, funds, equipment and nontechnical support staff. These were made available to the Central Machine Tools Institute, Bangalore and therefore it is, according to the papers presented in the Seminar, the only institution which is giving shape to the plans while in other cases, they are just paper plans, requiring the necessary incentives from the heads of the respective organisations. The fact that the librarians have plans, and also some of them are already rendering some services is an indication that the country is not lacking in talent but what is required is recognition, encouragement and proper utilization of their talents in the larger interests of the socio-economic development of the country.

Among the other related subjects on which articles were presented in the seminar are on budgeting, cost-benefit analysis of library and documentation services, library standards and survey of users needs.

Library budgeting has to go a long way before it can think of adopting modern methods in India. If initiation and continuation of library and documentation services are to be based on the outcome of cost-benefit analysis, possibly no library service can get a green signal. It is a well-known fact that almost all the internationally known secondary periodicals are being heavily subsidized by different institutions.

This is mainly because of the qualitative nature of the benefits derived by such services which cannot be measured in terms of quantity.

Library standards are good, if they are followed, at least by the relatively big libraries in India. Indian Association for Special Libraries and Documentation Centres (IASLIC) had standardized certain forms for use in libraries. It is doubtful whether its own members are following those set standards. However, it is good to realize the need for standards in libraries which may take concrete shape in times to come.

Periodical and systematic survey of users' needs will go a long way in keeping the selective dissemination of information service rendered by libraries up-dated. Practice of these professions will greatly enhance the prestige of the Indian libraries and librarians.

The DRTC had circulated the volume of papers contributed to the Seminar few days earlier to the scheduled date of the Seminar. This gives an opportunity to the delegates to attend the Seminar well-prepared. As all the papers were written mainly based on the individual experience in the special libraries in which they are employed, they give a bird's eye view of the problem of information dissemination with the proposed plan to meet the challenge. There is almost no problem which has not been touched—commencing from objectives and functions to the ultimate aim of providing information to the users pinpointedly, exhaustively and expeditiously in a manner most convenient to them at a reasonable cost with a view to securing an adequate conservation, utilisation and development of intellectual resources.

The volume of the papers is thus a good source of problems and solutions in the field of information retrieval in all fields of socio-economic life.

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Obituary

Prof. S. N. Bose, FRS

With deep sorrow, we record the demise of Prof. S. N. Bose. His passing marks the end of an era of Indian Science, an era of scientists of truly international repute, of names to conjure with, like C. V. Raman, J. C. Bose, P. C. Ray, M. N. Saha, H. J. Bhabha and S. S. Bhatnagar.

The chronological details of Prof. Bose's life are fairly well-known. Born in 1894 in Calcutta, he took his Master's degree in Mixed Mathematics in 1915, after a brilliant academic record securing the first position in all the examinations. Bose and his eminent colleague, Prof. M. N. Saha, then persuaded Sir Ashutosh Mukherjee, then Vice-Chancellor of Calcutta University, to open a Physics Department in the recently constructed Science College building, and jointly took charge of teaching physics and applied mathematics. In 1921 he joined the University of Dacca as a Reader in Physics. His third major scientific paper, the one which founded the science of quantum statistics, was written from there in 1923. Ironically, it was refused publication by the *Philosophical Magazine*, because it was so unconventional. Bose then sent it to Albert Einstein for his appraisal. The rest is now history, Einstein not only warmly appreciated it, but also took pains to translate it to German and publish it in the *Zeitschrift für Physik* in 1924. On the strength of an appreciative letter from Einstein, Bose could secure a visa from the German consulate and started for Europe in the same year. His first place of visit was, however, not Germany, but France, in the laboratory of Mme. Curie in Paris. This marked the beginning of a series of adversities for Bose.

To understand this statement, one must recall the situation in those days. India was then merely of colony of the British, where snakes and tigers supposedly roamed the streets in broad day light, it was the country of fakirs and magicians. The

occasional Rajahs and Princes could hope to get some recognition in Europe, but an Indian scientist was an anachronism. He could be patted on the back, but certainly he was not to be taken seriously.

The imperious Madame Curie refused to believe that Bose could speak French and ordered him to devote six months in learning the language before assigning him any work. In the one year that Bose spent with Mme. Curie, he had produced some fine experimental results on the piezoelectric properties of crystals, good work, but not exactly the type that one expects from the founder of quantum statistics. Then that was his assignment from Mme. Curie. The next year found Bose in Germany, in the company of Heisenberg, Jordan and occasionally with Einstein. There is no evidence that Einstein extended a helping hand then, as he had done earlier on receipt of the first paper. On the contrary, he appended an adverse comment to Bose's second paper on quantum statistics, which also he was gracious enough to translate and communicate to *Zeitschrift für Physik*. Einstein then proceeded to apply the statistics of photons in his own way and after some time lost interest in it.

We can well imagine the frustration that must have faced Bose then. Set adrift in the milieu of the scientific elite of Europe, he did not receive encouragement from any quarter. We shall never know why he did not enrol for a doctorate even. And then he had to return to India. The professor's chair at Dacca University was vacant. But he was not considered qualified enough for it. For a testimonial, Bose had to approach Einstein, who remarked with surprise, Are not your scientific papers testimonial enough?

After holding the Physics chair at Dacca University for a long period, Prof. Bose joined the University of

Calcutta in 1946 as the Head of the Dept. of Pure Physics and continued there upto 1956. In Calcutta, he soon became an institution in himself. Scientific workers from other disciplines came to him for advice. Bose had an uncanny depth and quickness of perception and his interests were broad enough to cover many widely separated domains of science. If one regrets the lack of intensity of his efforts in one particular branch of science, he had made it up by the extent of his interest, which made it possible for him to help workers from numerous specializations.

The subjects he taught at Calcutta University were X-ray crystallography and Relativity. However, his own plane of thought was so high, that routine teaching to post-graduate students must have held very little interest for him. It was during this period (1953-56) that he published his second set of papers, this time on Unified Field Theory, the solution of some equations which escaped even Einstein.

In 1956 Prof. Bose was invited to accept the Vice-Chancellorship of Vishwa Bharati University, a chair which he held for a little over a year. In 1958, he was elected a Fellow of the Royal Society, London. The same year, he was awarded the *Padma Bibhushan* by the Govt. of India, and appointed a National Professor. A section in the Indian Association for the Cultivation of Science, at Calcutta, was set aside for him. His last field of interest was the theory of numbers.

The most significant trait of Prof. Bose's character was the variety of his fields of interest. He was a theoretical Physicist, an experimentalist, a biochemist, a geologist, an archaeologist, a champion for propagation of scientific knowledge through mother tongue, all rolled into one. One wonders which way the posterity could have gained more, by intensive application of his intellect to

one particular field, or by this extensive browsing. It is more than possible that if he had received the proper encouragement in his early scientific career, his tangible contribution would have been much more

than only the Bose-Einstein Statistics. But then perhaps he would have been less the legend that he was during his own life time, who was supposed to be the panacea for any type of scientific problem.

It was a great satisfaction to all concerned that the grand ovation from the nation on Prof. Bose's eightyeth birthday did not come too late.

Dr. P. K. Ghosh

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Enquiries may be made with the Editor, TECHNOLOGY.

Notes & News

Lignite as Raw Material in Neyveli Fertilizer Plant

The fertilizer plant at Neyveli (South Arcot District of Tamilnadu) is first of its kind in the world which uses lignite as raw material. There were many deficiencies in the process selected, design, materials of construction and the plant layout. The contracts for the plant were signed in October, 1959, but actual production started in March, 1966 thus gestation period was about 6½ years. All the problems faced in this plant were unique in itself, the like of which was found nowhere.

The plant consists of following section.

(1) *Gasification Plant*: Raw lignite, 0.300 mm, containing 52.56 per cent moisture is conveyed through a system of belt conveyors from the mine to the raw lignite bunker in the fertilizer plant. From the bunker, the raw lignite is taken to a preparation section where it is crushed in hammer mills and screened into 0-8 mm and 8-40 mm fractions. The crushed lignite of 0-8 mm. size is dried to 6-8 per cent moisture in the two Buettner type turbo driers. The drying is done by means of a mixture of recy-

The hot exit gases from the generators are passed through superheaters to recover the sensible heat and then passed through waste heat boilers which generate steam at 18 kg./sq. cm. The steam generation is of the order of 21,000 kg./hr.

The gas leaving the waste heat boilers at around 230°C, and having a dust content of 100 mg per NM³ passes through cyclone separators where the major part of the coarse dust is removed by centrifugal force. The gas is further treated in three water spray scrubbers and cooled down to ambient temperature. The gas then undergoes final dust removal in centrifugal disintegrators. The gas with a maximum of 10 mg per NM³ of dust is then sent through dust filters to the gas purification plant. A 15,000 M³ floating type raw gas holder is installed in the line as a buffer.

The water used for dust removal and for cooling in the scrubbers and disintegrators is recycled after the slurry containing water and dust is processed in clarifiers.

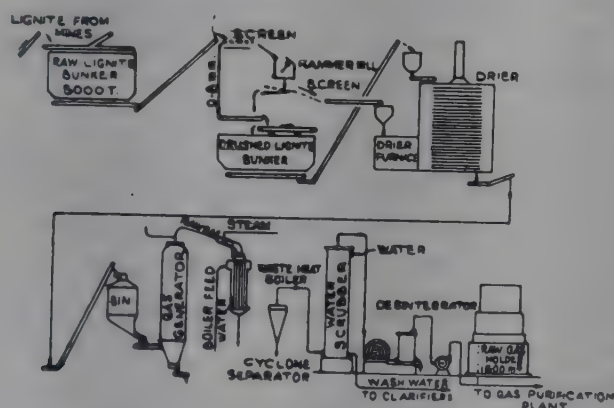
The rated production capacity and composition of the product from the gasification plant are given in Table 2.

Table 2—Rated production capacity and composition of product

Raw gas production 34,700 NM³ per hr.
Steam production 21,000 Kg. per hr.
Composition of gas:

CO	45.7 per cent
CO ₂	14.3 " "
H ₂	36.5 " "
CH ₄	2.4 " "
H ₂ S	4,000 mg./NM ³
S. Org.	400 mg./NM ³

(2) *Gas Purification Plant*: In this plant, raw gas drawn through dust filters from the gasification plant is compressed and processed to produce 91 per cent pure hydrogen which is sent to the air and gas fractionation plant and 98 per cent pure CO₂ which is sent to the urea plant.



Flow Diagram of Urea Plant Process at Neyveli

The physical and chemical characteristics of raw lignite are given in Table 1.

Table 1—Analysis of Raw Lignite
Proximate analysis:

	(per cent)
Moisture	51—56
Ash	22—33
Volatile matter	21.4 —24.93
Fixed carbon	19.1 —20.59
Calorific value, K. cal/kg.	2,560—3,150

Ultimate analysis:

	(Moisture-free basis)
Ash	4.84— 7.10
Sulphur	0.60— 1.00
Oxygen	17.97—21.20
Nitrogen	0.50— 0.78
Carbon	66.40—70.00
Hydrogen	4.53— 5.00
Ash fusion tempera- ture °C	1,260—1,410

cle gas and flue-gas (temperature 180-230°C) obtained by burning the 8-40 mm. lignite fraction in the drier furnace. The dried lignite from the driers is conveyed through Redler conveyors to the dried lignite bunkers from where it is fed to the Winkler generators.

Each of the Winkler generators is designed to make 13,000 NM³ of raw gas containing not less than 80 per cent CO+H₂. The Winkler gasification process is of fluidized bed type. The red hot fuel bed in the generator is kept in a state of turbulence by means of a gasification medium which consists of oxygen and steam. The lignite dust and gasification medium are intimately mixed so that heat is exchanged between the solid and gaseous ingredients involved in the reaction. The gas generators were originally designed to be operated at a temperature of 950°C.

The following steps are involved in it :

(i) Raw gas compression; (ii) H_2S removal by alkazid lye wash ; (iii) Co-conversion; (iv) Final H_2S removal by Vetrocoke lye and traces of CO_2 by NaOH and (vi) Final desulphurization by activated carbon.

Air Fractionation Plant : The air fractionation section consists of two Linde Frankl air separation units having a total output of 208,800 NM^3 of 98 per cent oxygen and 252,000 NM^3 of 99.56 per cent pure nitrogen per day.

Gas Fractionation Plant : In this plant, the carbon monoxide and methane present in the purified gas are removed to make the gas suitable for ammonia synthesis.

There are two identical units each with a normal output of 17,075 NM^3 per hr. of synthesis gas. The plant is part of the air fractionation plant and supplied by Linde of West Germany.

Ammonia Plant : The ammonia plant is designed with an on-stream efficiency of 330 days for a normal daily production of 285 tonnes of liquid ammonia and a maximum capacity of 300 tpd using the Fauser-Montecatini process.

The plant consists of the following sections :

- (a) Synthesis gas compression.
- (b) Ammonia synthesis.
- (c) Ammonia weighing, storage and liquefaction of vapour ammonia.
- (d) Vapour ammonia absorption and distillation.
- (e) Ammonia cylinder filling and testing.

Urea Plant : The urea plant consists of four loops and four converters. Each has a capacity of producing a maximum of 125 tonnes of urea per day. The reactors work at about 200 atmospheres and a temperature of $180^\circ C$. The process used is the total liquid recycle process of Montecatini. The plant produces prilled urea containing a minimum nitrogen content of 46 per cent.

Difficulties Encountered :

Raw Material : As plant is based on raw lignite the knowledge about gasification characteristics of it except proximate and ultimate analysis was vague. There was no pilot Winkler gasification plant available anywhere in the world to carry out tests. One had to go by the experience available with the vendors of the equipment, namely, Pintsch Bamag. It is well known that Winkler gasification was a well established gasification process and was operated in the German Democratic Republic for a number of years without much difficulty. The process was started with raw lignite but quickly switched over to a mixture of raw lignite and char fines and finally to char fines. However, the Neyveli plant was designed only for utilizing raw lignite keeping the operating temperatures of $950^\circ C$ prevailing in the working of Winkler generators in Germany but using char fines. No one foresaw the problem of benzene in the raw gas which became a serious difficulty, when the Winkler generators were operated at $950^\circ C$. Finally it was decided to operate the generators at around $1,250^\circ C$ which reduced or eliminated the benzene in the gas, thus making it possible to operate the gas fractionation plant without the condensation of the benzene. However, the operation of the Winkler generators itself at a temperature for which it was not designed posed many other problems. The refractories, the waste heat boilers, etc. were not designed for this high temperature and they suffered serious damage. Modifications of the refractory work, the tubes in the boilers, etc. had to be made. It has been recorded that normally Winkler generators give continuous uninterrupted operation of 160 to 200 days. The longest run was for 271 days. However, in Neyveli this has not been possible. The units required to be shut down within 10 to 60 days of start-up, mostly after shorter duration. The longest run was about 60 days or so.

Clinkering was another problem which forced generators to shut down for 2 to 3 weeks and made impossible to attain the rated capacity.

Process : 500 tpd urea plant in the year 1959 was biggest in the world at that time so the difficulties and problems could not be solved by any previous experience.

Plant Layout : There were several shortcomings in the layout of the plant itself which required much rectification after the plant was actually started. These rectifications had to be carried out practically in all the groups of the plant from the raw lignite preparation section to the urea prilling tower. This not only caused large number of design and operational problems but also resulted in lower production and interruption in the plant operation.

Materials of Construction : There were many instances in the plant where proper materials of construction were not used for the equipment. This has resulted in severe corrosion problems and replacement of the equipment in much shorter time than what was expected. This not only increased maintenance costs but also caused interruption to the operation of the plant resulting in lower production.

Cost of Operation : It is to be noted that the Neyveli plant has three gasifiers, two gas purification streams, three ammonia reactors and four urea loops for the production of 500 tonnes of urea. For a much higher capacity of urea, in a modern plant, there is only a single stream. Irrespective of the size of the stream, the maintenance problems are practically the same. Thus, the plant at Neyveli has four times the maintenance problems of a modern single stream plant but gives a much smaller quantity of the product. Added to this, being the first plant of its kind, it does not have the improvements that have taken place in the technology for the manufacture of ammonia and urea during recent years. Secondly, the consumption of raw materials and utilities in the plant are rather high. This makes the break-even point in the plant very high, probably in the range of 95-100 per cent. The production of urea in the fertilizer plant during the last few years is given in Table 2.

Table 2—Production of Urea in the Plant (te) (Rated Capacity of Urea—1,52,000 tonnes/annum)

Year	Material
1966-67	60,157
1967-68	72,743
1968-69	90,034
1969-70	91,695
1970-71	69,000
1971-72	42,938
1972-73	46,456
1973-74 (11 months excluding March'74)	29,000

[Fert. News, 19 (4) (1974), 8]

Basics of Organic Farming

Though chemical fertilizers are in large-scale use throughout the world, organic fertilizers and organic farming have not yet lost their importance. Even in America organic farming is getting popular. Sir Albert Howard, an English soil scientist who died in 1947 and who worked as Director of the Institute of Plant Industry in Indore, is the father of organic farming. The Green Revolution approach to increased food production is to maximize productivity of a given plot of land by growing improved varieties of plants and then supplying those plants with increased nutrients by means of artificial chemical fertilizers. Although the Green Revolution was not called that in the early 1930's the same principles were being applied then to a much smaller degree. Sir Albert felt that the best route to increased food productivity at moderate cost was to complete the cycle of life in the soil—especially to return to the land the organic by-products of crop production. Crop wastes, animal manures, garbage and even human wastes too properly treated to avoid disease problems should be returned to land. Like other soil scientists, Sir Albert had found that organic matter and humus were remarkably important to soil health. Continual and enthusiastic replenishment of soil organic matter could create a permanently productive kind of agriculture that did not need to rely on imports of fertilizer from outside the farm to maintain fertility year after year. He did recommend the use of mild and natural soil conditioners such as limestone and phosphate rock to

supplement the release of nutrients from the release of nutrients from the average soils impressive store of insoluble reserves. Of course, artificial fertilizers have advantages regarding their application and they restore to soils the levels of certain major minerals that are depleted. But the priority should be on the building of soil fertility more by completing the cycle of organic life and less by using fertilizers imported from other regions. By using synthetic fertilizers farmers can make more money than organic farming. But everywhere, including in America, farming situation is changing because all forms of production are changing. Soils rich in fertility, cheap energy sources and deposits of phosphate and other raw materials for fertilizers and industrial products are getting fast exhausted. In the light of these crises scientists have to think about new farming techniques. One result of this farming situation will be greater profit possibilities in the long run for farmers using the ecological principles that Sir Albert Howard outlined. As we reach closer to the bottom of the resource barrel, a system of farming that recycles more resources is bound to have tremendous cost advantages over one based more on using resources.

Organic farmers tackle the following situations :

1. *Insect and Disease Control*: Organic farmers rely on resistant plant varieties, cultural techniques and naturally occurring predators to control harmful varieties. Biological controls and old fashioned cultural methods may not be a completely effective control against pests. More research has to be done in this line.
2. *Pollution*: Recycling of sewage sludge and composted garbage to the land form an important part of organic farming programs which are, of course, not immune to its own pollution problems. However, some tests already completed show that, with reasonable care, return of sewage to the land is both practical and safe. Humus itself has significant

abilities to neutralize the effect of some toxic materials introduced into the soil.

3. *Feeding the Public*: Organic farming methods cannot feed all the people. Simply taking the chemicals and chemical fertilizers away from farmers is not the answer. But deemphasising synthetic and imported materials in farming, combined with other changes pointing toward a more ecological society, does stand a chance of creating a permanent, productive organic oriented agriculture.
4. *Nutrition is a farm-related problem*: There is controversy regarding nutritional contents in food produced by organic farming and farming done by synthetic farming. To claim that all organic food has superior nutritional value is not possible, because of the tremendous variation that exists in soils according to mineral content of soils and the way the plants are grown. Soil related nutritional problems of food produced and consumed deserves far more attention from scientists than it has received to date and possibly holds the key to the prevention of some chronic degenerative diseases. For example, we have known for a long time that iodine lack in the soil can be a cause of goitre, and there is now much evidence that people living in hard-water areas have a certain immunity to heart diseases. Who is to say that more such problems are not related to soil fertility, and that modifications along organic lines will not cause improvements? All the nutritional elements in food that influence human health have not yet been identified.
5. *Energy conservation is of growing importance*: As the cost of fossil fuel and energy, which are required to manufacture synthetic fertilizers, rises the present situation of cost of food product may also change. Profitminded farmers still look to synthetic fertilizers and pesticides for the means to stimulate production at least at present and in the near future. But there is a limit to

resources of all types. Organic methods provide a way to farm that makes maximum use of natural resources that are now wasted.

[Robert Rodale, Editor, *Crops and Soils*, 26 (3) (1973), 5.]

Pressure Gasification of Coal

The process of oxygen pressure gasification of brown coal was carried out commercially in Central Germany just before Second World War. After the war Ruhr Gas Co. and Lurgi extended this process to bituminous coal in an experimental plant at Holten; after successful experimentation a 1.2 mil. cu.m./day town gas plant by oxygen pressure gasification of weakly caking bituminous coals was constructed in Dorsten in 1954-55. It consisted of an oxygen plant with 2 Linde Frankl decomposition units each having a capacity of 6000 m³/hr. 6 coal pressure gasifiers with the corresponding waste heat boilers and lye heaters and a 3-line gas cooling system. This

was followed by the gas-cleaning system which consisted of 2 lines of a gas benzene washing plant using wash oil as washing agent, a cyanide washing plant which was operated with water and a hydrogen sulphide washing plant in which the alkazide process was used. This was followed by 3-line dry purification for the removal of residual hydrogen sulphide. A 2-line potash wash was used for the removal of CO₂. The pure gas had a calorific value of 3,800 K.Cal/m³ which had to be carburetted to a value of 4,600 K.Cal/m³ using natural gas. The resulting by-products, like tar, oil, phenol, hydrogen sulphide and ammonia, were processed into saleable products in the auxiliary processing industries.

Immediately after commissioning the plant, very strong corrosion was observed at the inside jackets of the gas generators, made of boiler plate; after running for 100 days the wall thickness was reduced more than half. A long search revealed that

chlorine was the cause of corrosion; chlorine reached coal through salt-containing water which is used in mining for dust prevention. This corrosion was prevented by steel plate lining with a material called Thermanit LM, having the following composition: 26 per cent Cr, 4.5 per cent Ni, 2.2 per cent Mo and 0.15 per cent C. By improvement of the grate and by controlling the corrosion, it was possible to obtain satisfactorily long operating periods with the gas generators. Over 300 days' operating periods between two repairs were quite frequent. By suitable construction it became possible to change worn-out parts during the operation, and increase production to 2 mil./m³ town gas/day.

The consumption values were most favourable when the operation was carried out at the highest possible temperature limited by the melting characteristics of the ash. At Dorsten a steam-oxygen ratio of 4 kg steam/m³ oxygen was obtained.

[*Fert. News*, 19 (4) (1974), 14]

News in Brief

Automated Method for the Determination of Direct Available P_2O_5

An automated photometric method for the analysis of direct available P_2O_5 in fertilizers has been developed. The method utilizes the basic Auto-Analyzer equipment along with a heating bath to destroy ammonium citrate and colouring matter and also to hydrolyze non-orthophosphates. The 0.15 and 0.35 mg. P_2O_5 /ml. ranges are expanded to read 10 and 90 per cent T, respectively, with a sampling rate of 30 analyses/hr. Experiments were conducted to show the effect of acid and ammonium citrate concentrations on colour development. The normality of acid needed to completely hydrolyze the phosphorus in non-orthophosphate samples was also determined. The results for samples of urea-ammonium polyphosphate, sodium pyrophosphate, sodium metaphosphate and ferric pyrophosphate, analyzed by the automated method, are reported and compared to results on the same samples analyzed by the official final action gravimetric quinolinium molybdo-phosphate method, 2.023-2.025; good agreement was shown between the methods. Six replicate determinations on 5 mixed fertilizer samples and a KH_2PO_4 primary standard by each method were in close agreement. The accuracy of the automated method was confirmed by analyzing 312 routine fertilizer samples by both the automated method and the gravimetric method; results did not show a significant difference when compared by Students' T-test at the 5% level.

[*J. of the AOAC*, 56 (5) (1973), 1079]

Heat Recycle Process for Urea Manufacture

The heat recycle process (HR), marketed by Technip, returns much of the heat of reaction into the process. The process is competitive as also the CO_2 conversion in the reactor takes place to the extent of 71-72 per cent. The urea synthesis reactor operates at an overall $NH_3:CO_2$ molar ratio of about 4:2:1. In the

process, the urea and unconverted carbamate containing reactor effluent is decomposed under low pressure to separate out carbamate and excess ammonia. The decomposed vapours are recycled to the reactor after condensation by indirect heat exchange with the reactor feed-streams which later produce steam. The steam generated is used to supplement steam going to the first decomposer. The process also features partial CO_2 feed to both stages of decomposition/absorption to save power, and an improved method of injecting air into the ammonia feed-stream instead of into CO_2 (for reactor passivation) to reduce the amount of inerts into the reactor. The steam requirement per tonne of urea in the HR process is only 0.64 tonne as compared with 1.2 tonnes in the conventional process. Electricity required per tonne of urea by this process is 115 kWh as compared with 145 Kwh in the conventional process.

[*Process Technol. Internat.*, 18 (11) (1973), 420]

Low Cost SNG from Heavy Feedstocks Using IGT Process

Deficiency of natural gas in United States which till yesterday was a paper prediction has become an uncomfortable fact today. Also, it is becoming evident that substitutes manufactured from light feedstocks will only play a limited role in easing the situation. The Institute of Gas Technology (IGT), Chicago, has evolved a process of producing SNG with a heating value of 930 Btu/ft³ for a price of 85 cents/m.m.Btu from a 120 m.m.cfd installation using Bunker C fuel oil (assumed price \$2/bbl) as the feed. The competitive price of the SNG product is due in part to the fact that the plant requires neither a separate hydrogen generating unit, although the process is one of hydrogasification, nor a methanator. Gasification is carried out in two fluidized bed reactors at a pressure of about 1,000 psig. In the first, the oil which has been warmed previously, reacts

at a temperature of 700°-760°C with a gaseous mixture of hydrogen and methane produced in the second gasification stage. The gas leaving the top of the hydrogasifier is substantially all methane and is separated from suspended solids, cooled and purified to remove aromatics and sulphur compounds. The char formed in the hydrogasifier next passes to a second fluidized vessel where it reacts with a mixture of superheated steam and oxygen which reforms it into a raw synthesis gas mixture of hydrogen, carbon oxide, methane and sulphur compounds at about 925°-980°C. The gas, then cooled to a temperature between 290 and 400°C, undergoes a shift conversion to transform the carbon monoxide into carbon dioxide which is then removed, along with some of the sulphur compounds, in a hot carbonate scrubbing system. After condensation of moisture and aromatic hydrocarbons, the gas is compressed and reheated before being fed to a hydrogasifier. The total fixed investment, including the cost of the oxygen plant, for a 120 m.m. sc.f.d unit is estimated as \$59.83 million.

Phosphoric Acid By the Kellogg-Lopker Process

When the Kellogg-Lopker process was first announced in 1968 it was estimated that savings in manufacturing costs of about 15 per cent would result. Now, after nearly four years operation of the first large scale plant at Marchon Division of Albright and Wilson Ltd., it has been shown that costs can be cut by as much as 25 per cent compared with conventional phosphoric acid processes.

Although the process is basically similar in principle to the conventional wet process the reductions in costs are due to the fundamental differences in the way in which the basic reaction is carried out, in the precise control of operation conditions, and in the equipment tailor-made for the new process. The

heart of the K-L process is a circulation loop reactor system controlled by an automatic sulphate ion analyser. The system consists of two vessels off-set vertically, but interconnected to form a recirculation system. Slurry is pumped from the lower vessel, the dissolver, into the upper vessel, the evaporator, and returns by gravity to the dissolver. The downward circulating flow of the reactor slurry through the system eliminates the possibility of any solids setting from the slurry. The main advantages of the whole system, i.e. rock preparation reaction and filtration, can be summarized as follows: (1) Reduced rock grinding requirements; (2) Reduced residence time in the apparatus; (3) formation of more uniform gypsum crystals resulting in higher filtration rates; (4) no moving internal parts in the reaction system; (5) minimal scale build-up and no sludge build-up.

The raw materials for the process are 78 per cent H_2SO_4 , Moroccan or Florida phosphate rock and crude fatty acid antifoam compound. The final products are gypsum and 32 per cent phosphoric acid.

Comparative operational details are given below.

Phosphoric acid recovery (percentage)	95	96
Operating manpower/shift	2-3	1-2
Power, kWh/ton acid	105	42
Cooling water, gal/ton acid	12,000	10,000
Steam, lb/ton acid	1,800	1,300
Maintenance costs as % of capital	9	6
Descaling shut-down	once/yr	once in 3 yr
Reaction residence-time, hr	7 to 8	2 to 2½

[*Process Technol. Internat.*, **18** (11) (1973), 421.]

Future of Coal

The oil crisis has provided long-term stimulus for the production of coal. For many countries having

coal producible at home there are now favourable prospects for its large scale use for production of liquid and pipe line gas under economically acceptable conditions. World production of coal outside China increased very slowly from 2004 in 1965 to 2076 million tons in 1972, but production in future will probably rise at an accelerated pace and could reach 3,500 million or more by 2000.

In USA progress in coal production has been severely retarded by clean air policies but the government now affords special priority to coal research; and the production may go up from 541 million tons in 1972 to at least 1300 mil. tons by 2000; the latter to include about 700 mil. tons for electricity generation, 280 mil. for conversion into gas, 220 for other internal uses (including liquefaction) and 100 mil. for exports. The established recoverable coal reserve could sustain about 300 years' production at the rate postulated for the year 2000 on the basis of present day conditions and without allowing for any further technological improvements.

In the USSR, production of about 1000 mil. tons is envisaged by 2000 compared to 652 mil. in 1972. Its recoverable reserves are considerably bigger than in the USA but they are largely concentrated in remote parts of Siberia. Elsewhere there are tentative plans to increase production; in Poland from 151 mil. tons in 1972 (excluding lignite) to 190-200 mil. in 1985, in S. Africa from 58 mil. tons in 1980 to about 200 mil. in 2000, in Australia from 54 mil. in 1972 to about 70 mil. in 1980 and in Canada from barely 16 mil. in 1972 to 71 mil. in 1990.

Conditions are less favourable, in western Europe, where most of the remaining reserves are at considerable depths in thin seams difficult of work. It has now been pointed out that with adequate investments, production could be maintained at the present annual level of about 300 mil. tons for at least 100 years. U.K. and W. Germany are now planning for higher coal consumption in power stations.

The world's coal/lignite reserves are estimated at over 8 mil. mil. tons coal equivalent amounting to well over 90 per cent of all fossil fuel reserves. It is estimated that considerably less than half total reserves will be technically recoverable. In addition, productibility is often greatly reduced by economic difficulties, notably by labour shortages.

Coal depends mainly on underground labour and was cheap only as long as miners were compelled by fear of unemployment to work for low wages under difficult conditions. By now, mining operations in the most advanced countries have been largely mechanized with consequent big reductions in labour requirement and substantial improvements in working conditions; but it remains difficult to recruit mine-workers in adequate numbers.

Regarding any method for overcoming the labour problems inherent in coal mining, Prof. M. W. Thring of UK has developed a 'telecheric mole mier', which in future should be able to cut its way into the seam and be steered by a human controller from the surface so that it follows the seam. UK's NCB is experimenting with automation devices with prospects of controlling mining operations from outside. The Coal Committee of U.N. Economic Commission for Europe says that after 1980 it may normally no longer be necessary for men to work at the coal face.

Underground gasification is another possibility of exploiting coal without underground labour and incidentally at a low environmental cost but all coal deposits will not be suitable for this process. US, USSR and W. Europe made widespread experiments on underground gasification during 1945-60. U.S. Bureau of Mines in cooperation with Rocky Mountain Energy Co. has a year ago drilled boreholes 400 ft down to a low sulphur coal deposit near Hanna. The experimental unit is able to handle upto 5.5 mil. cft/day, which could be used in power station; there are plans for its enrichment.

[*Petr. Econom.*, **41** (2) (1974), 61]

Patents*

Hydrated Crystalline Potassium Polyphosphate. N. E. Stahlheber (to Monsanto CO.). U.S. 3,723,602, Mar. 27, 1973, Appl. Mar. 8, 1971; 5pp. A slowly-soluble hydrated crystalline K polyphosphate of formula



wherein n is an integer > 10 , is described. A method of manufacture is disclosed based on the use of H_2O , a substantially H_2O -insoluble ammonium polyphosphate of formula



$$m/n = \sim 0.95 - 1.1, \text{ and } m_{\max} = n+2),$$

and a K source selected from KCl, K_2SO_4 , KNO_3 , K_2CO_3 , KOH, K phosphates, or mixtures thereof. In an example, 100 g of ammonium polyphosphate was slurried in 50 parts of H_2O at 25° and slowly mixed, with agitation, with 130 parts of a 45 per cent KOH solution. Ammonia was evolved and stripped from the slurry using N gas. The Product was recovered by filtration, washed, and dried. Its approximate composition was P_2O_5 52, K_2O 34, H_2O 14, and $N < 1$ per cent. Solubility in H_2O was < 0.1 g/100 c.c. at 25° . Essentially all of the P_2O_5 was citrate soluble.

[Fertilizer Abstracts, 6 (10), (1973), 238]

Concentrated Aqueous Nitric Phosphate Fertilizer. E. K. Drechsel and J. B. Sardisco (to Pennzoil Co.). U.S. 3,726,660, Apr. 10, 1973, Appl. Apr. 23, 1971; 6pp. Phosphate rock, or a solubilized form thereof, is reacted at $40-90^\circ$ with 20-40% of concentrator HNO_3 , based on the total amount of phosphate material, to form a reaction mixture. An aqueous $KHSO_4$ solution containing 10-50 wt% of $KHSO_4$ and 1-5 wt% of H_2SO_4 is prepared by reacting KCl and H_2SO_4 at $250-300^\circ$, followed by dissolution in H_2O . The $KHSO_4$ solution is then added to the phosphate reaction mixture in a controlled manner to facilitate crystal

growth and filterability of the $CaSO_4$ precipitate. Reaction is carried to complete acidulation at a dissolved solids content of 10-40 wt%. The $CaSO_4$ is separated and the resulting filtrate is contacted at $20-80^\circ$ with 1-10 wt% of NH_3 , based on the total wt of filtrate. Excess H_2O is evaporated and concentrated aqueous fertilizer product is obtained.

[Fertilizer Abstracts, 6 (10) (1973), 238]

Urea-Ammonium Nitrate Solution from Urea Production Effluent. E. R. Johnson (to Allied Chemical Corp.). U.S. 3,746,528, July 17, 1973, Appl. Apr. 20, 1971; 4pp. Aqueous urea- NH_4NO_3 fertilizer solution, with or without free NH_3 , is continuously produced from crude urea production effluent containing urea 35-52, NH_3 31-53, CO_2 1-3, and H_2O 10-16 wt% by neutralization of NH_3 in the effluent with aqueous HNO_3 . The NH_3 : urea ratio in the crude urea production effluent is reduced by vaporization of NH_3 . Then the urea effluent of lowered NH_3 content is fed into a neutralization zone where the HNO_3 is injected to react with essentially all of the NH_3 remaining in the effluent. During neutralization the reaction mixture is maintained in violent agitation at $125-40^\circ$, pH 6.5-7.5, and 1-3 atm absolute. Volatilized H_2O and CO_2 are removed and the aqueous urea- NH_4NO_3 solution is recovered from the neutralization zone. Hydrolysis of urea is substantially avoided. In an example the product contained urea 34.3, NH_4NO_3 45.6, and H_2O 20.1 wt%; 0.03-0.04 wt% of P_2O_5 as aqueous ammoniated superphosphoric acid containing N 10.2 and P_2O_5 34.2 wt% was added as a corrosion inhibitor. Other urea- NH_4NO_3 solutions containing free NH_3 26.0-28.0, NH_4NO_3 40.0-50.0, urea 12.0-15.0, and H_2O 12.0-17.0 wt%.

[Fertilizer Abstracts, 6 (10) (1973), 239]

Ammonia Synthesis System. L. E. Wright and A. E. Pickford (to C. F. Braun and Co.). U.S. 3,721,532, Mar. 20, 1973, Appl. Feb. 8, 1971; 7 pp. An apparatus and processing system are described for the synthesis of NH_3 from N and H. Two parallel

upright catalytic synthesis converters have mounted between them a heat exchanger with the piping installed so that the inlet and outlet of one converter and the inlet of the other converter are connected to the heat exchanger. By this arrangement feed gas may be passed in heat exchange relationship with partially synthesized gas from the first converter. One converter is mounted on the support platform and the other converter and the heat exchanger are mounted for movement with respect to the platform to accommodate dimensional changes caused by thermal expansion during operation. The system allows a simple compact arrangement of the equipment and insures proper synthesis temperature for effluent reaction.

[Fertilizer Abstracts, 6 (11) (1973), 262]

Removal of Ammonia from Waste Water. D. W. Breck. U.S. 3,723,308, Mar. 27, 1973, Appl. Nov. 16, 1970; 8 pp. Ammonium ions are selectively removed from aqueous solutions containing alkali and/or alkaline earth cations by cation exchange with zeolite F. This zeolite is a synthetic crystalline aluminosilicate having a $SiO_2:Al_2O_3$ mole ratio of $\sim 2 \pm 0.3$ which is derived from a K-rich reaction mixture. Examples show that zeolite F possesses unusually high cation exchange capacity and exceptional selectivity for NH_4^+ in the presence of interfering alkali and alkaline earth metal ions.

[Fertilizer Abstracts, 6 (11) (1973), 263]

Closed Pond System for Wet-Process Phosphate Plants. R. G. Hartig. U.S. 3,720,757, Mar. 13, 1973, Appl. Aug. 3, 1970; 6 pp. Fluorine values are removed from liquid effluents of wet-process phosphate plant complexes and the purified effluents are returned to the process for reuse. Silicon tetrafluoride in the effluents, by the addition of NaF, is converted to Na_2SiF_6 , which is separated from the effluent and calcined to form NaF and SiF_4 . The NaF is returned to the effluent stream and the SiF_4 is recovered as H_2SiF_6 by H_2O scrubbing. Addition of SiO_2 converts HF

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in the effluents to Na_2SiF_6 . Any H_3PO_4 in the effluents reacts with NaF and SiO_2 to form NaH_2PO_4 , which is separated from the Na_2SiF_6 as a liquid effluent stream. The NaH_2PO_4 is then treated with part of the SiF_4 formed in the calcination step to form H_3PO_4 . Since no H_2O solutions are discarded from the process, contamination of surface and ground H_2O is eliminated.

[Fertilizer Abstracts, 6 (11) (1973), 264]

Recovery of Acid Gases. A. J. Teller (to Teller Environmental Systems, Inc.). U.S. 3,721,066, Mar. 20, 1973, Appl. Dec. 29, 1970; 4 pp. Acidic components of a gas stream such as HF , SiF_4 , and SO_2 are removed by sorption at 100-400 °F and space velocity 10^2 - 10^7 /hr by nepheline syenite ore previously treated with 10-50 lb of H_2O /100 lb of the syenite and dried. In an example, 25 lb of nepheline syenite of 200-325 mesh particle size was treated with 8 lb of H_2O and dried to equilibrium with air at 200°F. The syenite was then blown into a baghouse having a filter area of 120 ft.², after which a gas at 110°F containing HF 100 and SO_2 80 ppm was passed at 250 ft³/min through the deposited solids on the surface of the bag filter. The space velocity in the bed of solids was ~42,000/hr. For the first 20 hr, the gas leaving the filter area contained $\text{HF} < 2$ and $\text{SO}_2 < 2$ ppm. During the period between 20 and 30 hr, the effluent gases contained $\text{HF} \sim 6$ and $\text{SO}_2 \sim 5$ ppm.

[Fertilizer Abstracts, 6 (11) (1973), 264]

Recovery of Phosphorus From Sludge. C. P. Orr (to Monsanto Co.). U.S. 3,743,700, July 3, 1973, Appl. May 13, 1971; 2 pp. Phosphorus sludge obtained as a byproduct in the production of elemental P by the electric furnace method is admixed with sufficient elemental P to provide a P : dirt ratio of at least 75 : 25 and continuously dried at > 100 to < 8 ft % H_2O . A dry, fluid sludge is produced that is readily recycled to the electric furnace.

[Fertilizer Abstracts, 6 (11) (1973), 264]

Ammonium Polyphosphate Liquid Fertilizer. T. V. Burns (to Amex Phosphates, Inc.). U.S. 3,734,708, May 22, 1973, Appl. Feb. 24, 1971; 6 pp. The title product, containing at least 50% of its P_2O_5 in the non-orthophosphate form, is produced in a mixing tee and its associated horizontal U-shaped reaction vessel. Impure wet-process H_2PO_4 containing 58-68 wt % P_2O_5 is fed at 200-220°F to the mixing tee concurrent with 0.8-1.2 moles of NH_3 /mole of P_2O_5 at 600-700°F; the retention time is ≤ 0.04 sec. The reaction mixture then enters the reaction vessel, maintained at 560°-600°F, where the reaction time is 0.10-0.18 sec. Molten ammonium polyphosphate leaving the reactor is immediately quenched with sufficient H_2O to form a liquid fertilizer solution containing N 11 and P_2O_5 37 wt %.

[Fertilizer Abstracts, 6 (11) (1973), 264-65]

Chloride-Free Potassium Phosphates. T. P. Hignett and A. J. Smith (to Tennessee Valley Authority). U.S. Patent Office Defensive Publication T914,007, Sept. 11, 1973, Appl. Oct. 10, 1972; 22 pp. A process is described for the production of Cl_2 , H_2 , and high analysis Cl-free K orthophosphate and K polyphosphate fertilizers. Saturated KCl brine and Hg are pumped into a Hg cell where the brine is electrolyzed to produce Cl_2 at the anode and K amalgam at the Hg cathode. Water and either orthophosphoric or polyphosphoric acid solution are fed to the decomposer unit where the amalgam is subsequently stripped of K in the production of H_2 gas and K phosphate solution, solids, or solution with solids. Decomposition is effected with or without short-circuiting elements in the decomposer. The spent brine is resaturated with solid KCl. The resaturated brine and the Hg recovered from the decomposed amalgam are recycled to the electrolysis cell. Stable K polyphosphate solutions as concentrated as 70% ($\text{P}_2\text{O}_5 + \text{K}_2\text{O}$) are proposed; a concentration of 62% plant food was attained in a stable K polyphosphate solution of pH 7.67 and density 1.740 g/ml at 25°C.

[Fertilizer Abstracts, 6 (11) (1973), 265]

Water-Insoluble Ammonium Polyphosphates. P. G. Sears and H. L. Vandersall (to Monsanto Co.). U.S. 3,723,074, Mar. 27, 1973, Appl. Jan. 18, 1971; 7 pp. The title materials have the empirical formula



where n is an integer of average value > 10 m/n is of average value between ~ 0.7-1.1, and the maximum value of m is $n+2$. These ammonium polyphosphates are prepared by heat treating at ~ 260° either (a) the reaction product of a condensed phosphoric acid and a combined ammoniating and condensing agent, (b) the reaction product of an H_3PO_4 and a combined ammoniating and condensing agent, (c) an ammonium orthophosphate and a combined ammoniating and condensing agent, (d) an ammonium pyrophosphate salt and a combined ammoniating and condensing agent, or (e) urea phosphate. Urea is the typical ammoniating and condensing agent. The products are useful as fertilizers, fire retardants, and builders in synthetic detergent compositions.

[Fertilizer Abstracts 6 (11) (1973), 266]

Reducing Dust Emission From Granular Fertilizers. J. E. Seymour (to Royster Co.). U.S. 3,734,707, May 22, 1973, Appl. Oct. 22, 1970; 6 pp. Conventional granular fertilizers, as they discharge from the cooler, are sprayed with aqueous solutions of N-containing salts to reduce dusting during subsequent handling, transport, and use. Commercial ammonium orthophosphate-ammonium polyphosphate solutions containing at least 10 wt % N, and N solutions containing NH_4 , NO_3 , ~ 44 and urea 35 wt % are applied at ~ 8-10 lb/ton of granular fertilizer. In an example, a 6-24-24 granular fertilizer was sprayed with 9 lb/ton of aqueous ammonium orthophosphate-ammonium polyphosphate solution containing N 10 and P_2O_5 34 wt %. Particulate emission from the treated product was only 41.7% of that from the untreated product.

[Fertilizer Abstracts, 6 (11) (1973), 266]

Inhibition of Corrosion in Hot Carbonate Units for Removal of

Carbon Dioxide. Z. A. Foroult and B. E. Hopkinson (to Esso Research and Engineering Co.). U.S. 3,721,526, Mar. 20, 1973, Appl. July 17, 1970; 3 pp. Corrosion of C steel by air-saturated alkali metal carbonate solutions of ~25 wt % or greater concentration, such as those used to scrub CO_2 from NH_3 synthesis gas mixtures, is greatly reduced by adding to the scrubbing solution at least ~1.5, preferably 2-5, wt % of an alkali metal nitrite such as KNO_2 .

[Fertilizer Abstracts, 6 (12) (1973), 287]

Phosphorus and Steel From Iron-Containing Phosphate Rock. Leonard Seglin and C. A. Gray (to FMC Corp.). U.S. 3,734,717, May 22, 1973, Appl. Nov. 18, 1971 4 pp. Phosphate rock is continuously melted together with recycled slag and a flux, if necessary, in an oxidizing zone at least 225°F hotter than the reducing zone which is physically separated from the oxidizing zone. The molten material is continuously pumped from the oxidizing zone into the reducing zone where reaction with C takes place to produce elemental P and Fe. Molten slag from the reducing zone is in part recirculated to the oxidizing zone and in part removed from the process. The elemental P is recovered by condensation; ferrophosphorus is transferred to the oxidizing zone where P is preferentially oxidized and steel is recovered from the bottom of the oxidizing zone.

[Fertilizer Abstracts, 6 (12) (1973), 288]

Phosphoric Acid Manufacture. Bernard Bigot (to Produits Chimiques Pechiney-Saint-Gobain and Union Chimique-Chemische Bedrijven). U.S. 3,755,539, Aug. 28, 1973, Appl. Jan. 2, 1970; 6 pp. A two-stage process is described for producing H_3PO_4 from phosphate rock by acidulation with H_2SO_4 . In an example, 100 parts of finely ground Moroccan phosphate was continuously mixed with 95-112 parts of 93% H_2SO_4 preliminarily mixed with dilute H_3PO_4 . The reaction mass in this first reaction vat was maintained at 70° and contained ~36% solids. A part of the reaction

mass continuously flowed into a second reaction vat containing 25 g of H_2SO_4 /l. and enough phosphate rock to react with excess H_2SO_4 from the first stage. Wash liquor from the gypsum filter and a portion of the H_3PO_4 were recycled to the first reaction vat. Residence times in the first and second reaction vats were 5 hr-40 min and 1 hr-10 min, respectively. The overall recovery of P_2O_5 was 99.1%.

[Fertilizer Abstracts, 6 (12) (1973), 288]

Phosphoric Acid. W. C. Klingelhofer and J. E. Sansing (to Allied Chemical Corp.). U.S. 3,723,606, Mar. 27, 1973, Appl. Dec. 21, 1970; 10 pp. Wet-process H_3PO_4 of low CaCl_2 content is produced by acidulation of phosphate rock with HCl in the presence of 3-10 wt parts of NaCl /100 wt parts of phosphate rock. After removal of insoluble siliceous material, a clear aqueous acidulate of H_3PO_4 and CaCl_2 containing ≤ 0.1 wt% of SiO_2 and 125-135 g/l. of P_2O_5 is produced. This acidulate is then extracted countercurrently in ~9-16 stages at ~25-80° with an organic liquid containing isobutyl alcohol ~75-85 and heptane ~25-15 vol % in the presence of ≥ 0.9 wt part of added HCl per wt part of P_2O_5 ; 3-5 vol parts of extractant is used/part of acidulate. The resulting organic solution of H_3PO_4 containing HCl and ~1-6 parts of Ca /100 wt parts of P_2O_5 is then extracted countercurrently in 2-9 stages at 25-80° with aqueous H_3PO_4 recycled from the process, followed by extraction in 7-14 stages at ~25-80° with H_2O . After concentration of the resulting aqueous H_3PO_4 by evaporation to remove the HCl and part of H_2O , an aqueous concentrated H_3PO_4 containing ~0.05 wt part of Ca /100 wt parts of P_2O_5 is produced.

[Fertilizer Abstracts, 6 (12) (1973), 288]

Slow Release Fertilizers Having a Constant Release Rate. H. J. Sommer et al (to Shell Oil Co.). U.S. 3,748,115, July 24, 1973, Appl. Nov. 16, 1971; 11 pp. The title product, formed in the shape of a right cylinder 0.75-6 in. long and 0.75-2.5 in.

in diameter with a minimum bulk vol of 0.30 in.³ consists of one or more plant nutrients uniformly dispersed in a hydrophobic matrix partially coated with the same hydrophobic material so that the ratio of uncoated surface area to the total vol of the cylinder is in the range of 0.025-3.00:1. The hydrophobic matrix and coating is composed of asphalt and one of the following materials: 0-20% petroleum wax, 0-20% cutting stock, 0-20% of a mixture of petroleum wax and cutting stock, 0-50% blowing flux, or 0-75% gilsonite, all percentages being based on the wt of asphalt. Surface coatings are applied so that either one or both ends or a lengthwise strip on the periphery of the cylinder remains uncoated. Examples of H_2O and soil leaching tests show near constant nutrient release from the products.

[Fertilizer Abstracts, 6 (12) (1973), 293]

Ammonium Nitrate Neutralizer. T. M. Cook, G. L. Tucker, and M. L. Brown, Jr. (to Mississippi Chemical Corp.), U.S. 3,758,277, Sept. 11, 1973, Appl. June 11, 1971; 6 pp. A thermal siphon-pressure pump neutralizer is described for production of NH_4NO_3 from NH_3 and HNO_3 . Evolution of NH_4NO_3 smog in the exhaust gases leaving the neutralizer is minimal; no auxiliary scrubbing equipment is required for treatment of these gases. The neutralizer consists of a vertical cylindrical vessel having an axially-mounted NH_3 inlet in the bottom, a side-mounted HNO_3 inlet, and an axially-mounted exhaust gas outlet in the top. Within this vessel is another concentrically mounted vessel having an open top and bottom. The annular space between the two vessels serves as a first reaction zone which is contiguous with the inner vessel that serves as the second reaction zone. Circulation occurs between the two vessels. Concentration of HNO_3 in the first reaction zone, to which the HNO_3 is fed, is $< 15\%$ and preferably $< 0.5-1\%$ HNO_3 . Most of the HNO_3 is neutralized with NH_3 in the second reaction zone. The resulting solution is removed from the second reaction zone, recirculated to the first reaction zone, and recovered as NH_4NO_3 .

product. Circulation for the process is facilitated by a thermal siphon and pressure effect caused by the exothermal heat of neutralization of HNO_3 with NH_3 in the second reaction zone and by the density differential between the product solution and the reaction solution. A curvilinear deflector is mounted above the discharge of the second reaction zone to divert downward to the first reaction zone the discharging fountaining solution. A mesh mist eliminator in the neutralizer vapor discharge removes entrained liquid from the exhaust gases and permits the liquid to drip back into the first reaction zone. Examples indicate that NH_3 , NO_x losses in the exhaust gases are $< 0.1\%$ when the unit is operating with reasonable efficiency.

[Fertilizer Abstracts, 7 (1) (1974), 1]

Synthesis Gas. M. J. P. Bogart (to Fluor Corp.). U.S. 3,743,488 July 3, 1973, Appl. May 27, 1971; 6 pp. High-pressure synthesis gas containing H_2 and CO_2 is produced by reaction of steam with hydrocarbon vapor. The reactants are heated to the reaction temperature of $> 750^\circ\text{F}$ and then reacted adiabatically at > 700 psig with the catalyst in a separate reaction zone. The two-step reaction process is repeated at successively higher temperatures and pressures until the hydrocarbon vapor has been exhausted and a high-pressure synthesis gas is obtained. Separation of the heating and catalytic reaction steps avoids equipment-imposed limitations on high pressures in the reaction apparatus at reforming temperatures and allows higher pressure output synthesis gas. Use of convection heat to heat the reaction mixture in the lower temperature portion of the reforming reaction results in significant fuel savings.

[Fertilizer Abstracts, 7 (1) (1974), 2]

Urea Synthesis. Ivo Mavrovic U.S. 3,759,992, Sept. 18, 1973 Appl. June 29, 1970; 18 pp. Urea is produced by the reaction at ~ 320 - 430°F and ~ 1500 - 4500 psig of NH_3 , CO_2 , and ammonium carbamate, proportioned in amounts of 3-6 moles of total

equivalent NH_3 /mole of total equivalent CO_2 . From 10-100% of the fresh CO_2 feed stream to the reactor, an amount equivalent to the stoichiometric quality of urea formed in the reactor, is reacted at 10-670 psig with NH_3 in the presence of urea and H_2O to produce an aqueous ammonium carbamate solution. This solution and the balance of the fresh CO_2 is then charged to the reactor for the formation of urea in a total recycle process having improved NH_3 and heat recovery.

[Fertilizer Abstracts, 7 (1) (1974), 3]

Recovery of Fluorine in Production of Wet-Process Phosphoric Acid. E. N. Case (to Atlantic Richfield Co.) U.S. 3,743,725, July 3, 1973, Appl. Nov. 4, 1971; 8 pp. Continuation-in-Part U.S. 3,619,136 (FA 5,345). Fluorine-containing phosphate rock is digested at $< 180^\circ\text{F}$ with H_3PO_4 containing 20-25% P_2O_5 to produce insoluble solids and a CaHPO_4 - H_3PO_4 - H_2O solution $\sim 90\%$ saturated with CaHPO_4 ; at least 90% of the $\text{Ca}_3(\text{PO}_4)_2$ in the rock is solubilized. The wt ratio of acid P_2O_5 :rock P_2O_5 is $\leq 7:1$. After removal of the insoluble material, the solution is treated with H_2SO_4 to produce H_3PO_4 and precipitate CaSO_4 which is then removed. Cooling of the H_3PO_4 to 70 - 95°F causes precipitation of the fluorine values in the form of solids, containing 20-40 wt % of F, which are removed. Part of the purified H_3PO_4 is then removed as product. The remaining H_3PO_4 is reheated to digestion temperature and recycled to the digestion stage where it solubilizes F from the phosphate rock for repetition of the F recovery cycle. Since the recovered F values contain little SiO_2 , the material can be used to produce HF.

[Fertilizer Abstracts, 7 (1) (1974), 3]

Removal of Cationic Impurities from Wet-Process Phosphoric Acid. Klaus Frankenfeld and Gatzmann (to Chemische Fabrik). U.S. 3,764,657, Oct. 9, 1973, Appl. Ger. Oct. 14, 1970; 3 pp. Ammonia, NH_4OH , or ammonium salts are added to technical grade wet-process H_3PO_4 along with isopropanol to precipitate the impurities which are

then separated. The resulting filtrate is passed through a highly acidic cation exchange resin in the H^+ form to remove the alkali or ammonium salts. Isopropanol is then distilled from the filtrate to produce the purified H_3PO_4 . In the process, 0.06-0.12 moles of alkali ions are used per mole of P_2O_5 in the acid. The amount of isopropanol added is 2-5 times the amount of raw H_3PO_4 , but $< \sim 30$ vol %.

[Fertilizer Abstracts, 7 (1) (1974), 3]

Phosphate Fertilizers. E. A. Majewski (to Phosphate Co-Operative Co. of Australia, Ltd.). Australian 433,269, Mar. 2, 1973, Appl. Nov. 20, 1968; 28 pp. Phosphate rock is acidulated with 20-40 wt % excess H_2SiF_6 at 60 - 105° to produce a mixture of H_3PO_4 , H_2SiF_6 , CaSiF_6 , and a precipitate of relatively insoluble hydrated CaSiF_6 . The precipitate is removed by filtration and the remaining filtrate is heated to concentrate the acids therein. The mixture resulting from heating is then defluorinated by reaction with SiO_2 at 80 - 120° . Silicon tetrafluoride evolved during the defluorination step is absorbed in H_2O to recover F as H_2SiF_6 which is recycled for reaction with further phosphate rock. By this process $\text{CaH}_4(\text{PO}_4)_2$, H_3PO_4 , or a mixture of $\text{CaH}_4(\text{PO}_4)_2$ and H_3PO_4 , which can be used in the production of NPK fertilizers of high analysis, is produced. Examples indicate that the products contain 53.1-56.1% total P_2O_5 .

[Fertilizer Abstracts, 7 (1) (1974), 3]

Electrolytic Production of Chlorine, Hydrogen, and Concentrated Alkali Metal Phosphate Solutions. Jean-Louis Butre and Francois Pierrot (to Progil). U.S. 3,763,005, Oct. 2, 1973, Appl. Ger. May 15, 1970; 5 pp. The title process is carried out in an electrolytic cell having a permselective membrane separating the anodic and cathodic compartments. This membrane is made of a polymer such as polytetrafluoroethylene with sulfonic groups, which has good resistance to Cl_2 and alkaline agents. The porous anode is constructed of Ti or a Ti-group metal having a Pt, Pt alloy, or Pt oxide coating on its active surface

opposite the membrane and the cathode, which is made of porous Ni. Aqueous alkali metal chloride solution, for example NaCl, is force fed into the cathodic compartment. At the same time concentrated wet-process H_3PO_4 or a concentrated aqueous alkali metal phosphate solution is force fed into the anodic compartment. Anolite electrolyte is thereby forced to percolate through the porous anode preventing Cl_2 from escaping into the space between the anode and the permselective membrane. The Cl_2 is continuously collected from the anodic compartment the H_2 and concentrated alkali metal phosphate solution, for example $Na_3P_3O_{10}$, are continuously removed from the cathodic compartment. Examples indicate that pure H_2 is produced. Chlorine of 99% purity is evolved; it contains CO_2 0.5, O_2 0.5, and H_2 < 0.02%. The alkali metal phosphates produced contain < 0.3% of the corresponding chloride.

[Fertilizer Abstracts, 7 (1) (1974), 5]

Phosphorus Pentoxide. Lothar Reh and Carl-August Maelzer (to Metallgesellschaft A.G. and Deutsche Babcock & Wilcox A.G.). U.S. 3,767,768, Oct. 23, 1973, Appl. Ger. Feb. 27, 1971; 6 pp. See Ger. Offen. 2,109,350 (FA 6,712).

[Fertilizer Abstracts, 7 (2) (1974), 29]

Ammonium Polyphosphate from Superphosphoric Wet-Process Acid. R. S. Meline (to Tennessee Valley Authority). U.S. 3,775,534, Nov. 27, 1973, Appl. Nov. 15, 1971; 11 pp. Continuation-in-Part U.S. Patent Office Defensive Publication T896,056 (FA 5,913). Stable liquid fertilizers containing 80-96% of the total P_2O_5 in polyphosphate form are made from wet-process superphosphoric acid containing 10-50% polyphosphate, preferably 20-25 wt %. Condensation of ortho P_2O_5 in the acid to pyro P_2O_5 and more-highly condensed forms of polyphosphates is accomplished by the heat of reaction of NH_3 and the acid in a simple pipe reactor at atmospheric pressure and 630-700°F. The resulting melt is quenched in cooled liquid fertilizer where the additional NH_3 for the desired N : P_2O_5 ratio is fixed

and H_2O is added to produce the desired grade of liquid fertilizer, which is at least 10-34-0. Polyphosphate species distribution in this product is 25-32 wt % pyrophosphate and 48-60 wt % of more-condensed polyphosphates. All or part of the wet-process superphosphoric acid may be replaced by electric-furnace superphosphoric acid. Alternatively, the melt leaving the pipe reactor may be solidified into a friable solid suitable for granulation by cooling to ambient temperature.

[Fertilizer Abstracts 7 (2) (1974), 30]

Coal Gas Plant Near Calcutta

A coal gasification plant to produce 15 million cubic feet of pipeline gas a day for domestic and industrial use will be set up in Dankuni, 9 km. from Calcutta. The Coal Mining Authority (CMA) has approved the feasibility report prepared by the Engineering Projects India (EPI) on the gasification plant. The plant would come into operation within 36 months from the time EPI gets the Rs. 14 crores contract from the CMA. Once gas starts flowing through pipeline, this plant would save 200 tonnes of kerosene a day. Two-thirds of the gas produced would be used by industries and only about 5 million cu. ft. might be available for home use.

This plant will yield every day 800 tonnes of coke and 100 tonnes of tar and from the latter 5 tonnes of cresols and phenols will be extracted.

NCST Projects

An outlay of Rs. 180 crores for about 50 projects have been proposed by the National Committee on Science and Technology in the field of fuel and power. Setting up of two low temperature carbonization plants and producing smokeless fuel for domestic use have been recommended. A prototype coal-to-oil plant producing half-to-one million tonnes of oil products per year and also programmes for gasification of coal to meet the industrial and domestic demands have also been proposed.

Fertilizer Plant at Paradeep

Sri K. C. Sharma, Chairman and

Managing Director FCI Ltd., while addressing a news conference on the eve of the foundation laying of the Rs. 250 crores fertilizer project at Paradeep (Orissa) by the Prime Minister, said on March 31, 1974 that this project would be the largest single fertilizer complex in the country. This will be FCI's twelfth fertilizer plant and will have an annual output of 7,61,200 tonnes in terms of three essential plant nutrients, viz., nitrogen (3,11,200 tonnes) phosphorus (3,00,000 tonnes as P_2O_5) and potash (1,50,000 tonnes as K_2O). Apart from the fertilizer plant, the complex includes a soda ash and an ammonium chloride plant to be set up at an estimated cost of Rs. 25 crores. Foreign exchange component of the fertilizer plant will amount to Rs. 55 crores and that of the soda ash and ammonium chloride to Rs. 10 crores. The French tie-up for a loan of 300 million francs had been finalized but equipment, designs and contracts are yet to be finalized. The project will have a single stream ammonia plant of 1,350 tpd capacity based on fuel oil as feedstock and a 1,350 tpd urea plant in single stream. It will produce 14,42,880 tpy of two types of complex fertilizers with 28-28-0 and 17-17-17 formulations besides urea, which are estimated to contribute to an additional 7.5 million tonnes of foodgrains annually. Orissa Government would provide as much land as would be necessary at a premium of Rs. 2,000/acre near the deepest draft port of Paradeep. The project will require 25 mgd of water and 70 MW electricity. The State Government, in addition to electricity and water, would provide an 18-mile long embankment along river Mahanadi for the protection of plant and ancillary industries in urea. Coal, another raw material, will be made available from the neighbouring Talchar coal-fields which are well connected with Paradeep by road and rail. The project will provide direct employment to about 2,000 persons and will help further in alleviating the unemployment among the local people with the generation of ancillary industries and trade activities. The project is expected to go into production in 1978.

Giant Fertilizer Plant in Phulpur (U.P.)

Prime Minister Smt. Indira Gandhi laid the foundation stone of South Asia's biggest fertilizer plant at Phulpur near Allahabad (U.P.) on 16th January 1974. Estimated to cost about Rs. 120 crores, this plant will have a capacity of 900 tonnes per day of ammonia and 1,500 tonnes per day urea based on fuel oil as feedstock. It is expected to go into production by the end of 1977. The plant is being set up by the Indian Farmers Fertilizer Co-operative Ltd. (IFFCO). It will require foreign exchange worth Rs. 50 crores which is expected to be made available by the World Bank. When completed, the plant will employ about one thousand people and go a long way in improving the economic condition of the farmers of eastern Uttar Pradesh.

[I. P. S. Bull., 23 (75) (1973), 1]

Fertilizers Deal with USSR

India has entered into a contract with the Soviet Union for the supply of 325,000 tonnes of fertilizers of three different varieties worth Rs. 58 crores. The contract to this effect has been signed at New Delhi on 28th January 1974 between the representatives of the Minerals & Metals Trading Corporation and Soviet Trading Organisation.

The fertilizers to be imported from the Soviet Union will comprise of 200,000 tonnes of urea, 75,000 tonnes of ammonium sulphate and 50,000 tonnes of muriate of potash. The supplies are expected to start in March this year and will be completed by December 1974. The fertilizer's price would be paid for by goods exported to the Soviet Union under the Soviet trade plan for 1974. This contract is considered 'very significant' among the MMTC officials circle particularly when urea is not available in the world market now.

R & D Efforts in the USA

The total number of scientists and engineers engaged in R & D has declined from 5,60,000 in 1969 to 5,25,000 in 1972 in the USA, according to a report published in 1973 by National

Science Board, USA. Two third of the US total R & D personnel in 1972 were engaged in industry while the Federal Government and Universities had 13 per cent each. Out of the total expenditure of 28 billion dollars in 1972, 55 per cent were spent by Federal Government, 40 per cent by private industry and the Universities and colleges spent another 4 per cent. The proportion of the Gross National Product (GNP) spent for R & D, dropped from 2.9 per cent in 1963 to 2.6 per cent in 1971. However, during the same period it rose from 2.3 per cent to 3 per cent in USSR and it increased from 1.4 per cent to 1.8 per cent in Japan. In India, it has also shown an increase from 0.21 per cent in 1958-59 to 0.43 per cent in 1969-70.

The Federal Government's expenditure in 1972, was spent as follows (%): national defence, 54; space exploration, 19; health, 9; advancement of science and technology, 4; transportation, 4; environment, 3; and energy development, 2.5. Taking all the sectors together, two-thirds of the total money spent for R & D was for development activities, 22 per cent for applied research and 14 per cent for basic research. There was a significant change in the share of the total basic research expenditure used by different sectors in the period 1960-72. The Universities increased their share from 43 to 57 per cent while industry's share has almost remained the same (about 20%).

In India, public sector provides about 94 per cent of the expenditure on scientific research while the share of the private sector is of the order of six per cent only. Private industry is just spending about 1 per cent of its total turn-over on R & D. On seeing the sectorwise distribution of R & D expenditure in India we find that agriculture and animal husbandry account for one-third of the total R & D expenditure and industrial research accounts for only a quarter.

[Tech. Manpower, 15 (12) (1973),]

Slagging Process for Gasifying Coal

The British Gas Corporation is preparing for a commercial test of its high pressure slagging process for

gasifying coal. The plant in Westfield, Scotland, that has been successfully demonstrating the commercial feasibility of upgrading to pipeline the 300-400 Btu gas produced by Lurgi process, was scheduled to be closed as the plant's service area is converted to use North Sea gas but will instead be modified to test the slagging process. The \$10 million project, aimed at reducing coal gas production cost, will be funded by 14 U.S. firms. Operation is planned for 3 years. British Gas Corporation developed the slagging process over 10 years ago but never carried it out beyond the pilot plant stage.

[IGT Highlights, 4 (9) (1974), 2]

World Fertilizer Fund

The 30th annual session of the ECAFE held in Colombo in the last week of March 1974 adopted a resolution seeking to establish a world fertilizer fund to assist the developing countries to procure supplies at reasonable rate and to help expand fertilizer production. The proposal, mooted by Ceylon's Prime Minister, Mrs Sirimavo Bandaranaike, in her inaugural address to the session, met with the unanimous approval of the plenary session of the Conference. The resolution takes note of the fact that ECAFE region's population constitutes over half of the mankind and the majority of the people in these areas are living at a bare subsistence level, beset with grave food scarcity, rapidly increasing food prices, resulting in malnutrition and threat of starvation. The resolution called upon the Executive-Secretary to consult immediately with the relevant international organizations and with member-governments with a view to formulating for consideration by the coming world food conference, concrete proposals for establishing a world fertilizer fund to assist developing countries to procure supplies at reasonable prices and to help expand fertilizer production.

Award

Dr. R. Choudhuri, Technologist, Physical Research Wing, P & D Division, Sindri, has been awarded Prof. N. N. Chatterjee Medal for the year 1973 by the Asiatic Society of

India for his significant contributions in the field of Economic Geology with special reference to the phosphatic minerals. The society, which makes a number of awards periodically to scholars of eminence from India and abroad on specified fields of Science and Arts, presented the above medal to Dr. Choudhuri at their Annual General Meeting held at Calcutta on 4.2.74. Besides to Dr. Choudhuri, a number of other awards were also made on 4.2.74, notable amongst whom were to Prof. Linus Pauling of Caltech (Nobel Laureate); Prof. T. Burrow of Oxford University; Dr. Louis Dumont, Director, Studies Ecole Pratique des Hautes Etudes; Dr. D. N. Kundu, Director, Saha Institute of Nuclear Physics; Dr. S. Sen, Director, Institute of Historical Studies and Dr. B. K. Aikat, Professor of Pathology and Microbiology, Post-Graduate Institute of Medical Research Centre, Chandigarh.



Dr. R. Choudhuri

Dr. Choudhuri, after joining FCI Ltd., obtained his Ph.D. from Calcutta University in 1973 for his work on the phosphatic deposits in Visakhapatnam area. In this work, investigations were carried out on the structural framework of the area, petrology of the constituent rock units, backed by extensive petrochemical analysis, the nature of the apatite (an important source of phosphate) bearing pegmatites with spe-

cial reference to their mineralogy, plausible mechanism of the phosphate fractionation from the source melt, nature of the source melt or magma (carbonate *vis-a-vis* pegmatite) and the structural control on the ore localisation. The techno-economic aspects of the phosphate deposits were also studied at length.

Dr. Choudhuri has also carried out extensive mineralogical work on almost all the known Indian phosphate deposits. It may also be mentioned that although analytical reports covering phosphatic resources of India were available as early as in the late 19th century, Dr. Choudhuri was the first Indian geologist to report the occurrence of phosphorite in the Kumaon-Himalaya belt [*Technol.*, 3 (1966), 319] and thus focus the attention for the subsequent findings of phosphorite horizons of economic significance in identical set-up. Besides phosphates, Dr. Choudhuri also participated in a number of major exploration work on gypsum (Mohangarh and Nagaur gypsum deposits of Rajasthan), pyrites and potash.

Dr. Choudhuri has a number of important publications to his credit.

Our heartiest congratulation to him for his achievements and rare distinction.

Indo-German Fertilizer Promotion Project

Fertilizer Corporation of India Ltd., which has pioneered and developed nationwide facilities in fertilizer promotion and agricultural research, has been selected as the Indian counterpart for the Indo-German Fertilizer Educational Project. This project, launched at Rukmindanga, Dt. Nadia W. Bengal, on Feb. 4, 1974, was inaugurated by the Chief Minister of W. Bengal, Sri S. S. Ray. Sri Abdul Sattar, Minister of Agriculture, W. Bengal, expressed special satisfaction that this promotional and educational programme is being dove-tailed into the extension programmes of the State Government, so that these become complementary and supplementary to each other.

The primary objectives of the programme included popularising com-

plex ANP (ammonium nitrate phosphate) among the farmers, promoting balanced use of fertilizers and increasing the level of fertilizer consumption per unit of cultivated area. The programme would be spread into the districts of Nadia, 24-Parganas, Hooghly, Bankura, Murshidabad, Malda and Purulia. Criteria for selection of area to implement the project included the present level of consumption of NPK; percentage of irrigated area, percentage of area under high-yielding variety programme, potentiality to consume higher levels of NPK; and soils and crops suited to the use of ANP.

[*Fert. Digest*, 12 (2) (1973-74), 7]

Assistance to Iraq

Fertilizer Corporation of India Ltd. has entered into a technical assistance agreement with the State Organization of Industrial Design and Construction, Ministry of Industry, Government of Iraq, under which FCI will provide technical experts for designing, construction and fabrication of new fertilizer plants in Iraq. This agreement, first of its kind to be signed by FCI with any foreign Government, is a part of the overall Indo-Iraq Technical Assistance Agreement.

[*Fert. Digest*, 12 (2) (1973-74), 9]

FCI-FAO Collaboration

The Fertilizer Corporation of India and the Food & Agriculture Organization of the UN are collaborating in fertilizer experiments promotion programme. Under this programme the following two projects are being implemented: (i) popularizing complex nitrophosphate fertilizers amongst the farmers in U.P.; and (ii) evaluation of the relative efficiency of sulphur-coated urea under Indian agroclimatic conditions. FAO is supplying 10.5 tonnes of sulphur-coated urea to FCI for this project. The results of these trials will be evaluated jointly by FAO experts and the FCI scientists. The scheme for popularizing nitrophosphate is being financed by the Freedom from Hunger Campaign of FAO, FCI and U.P. Government.

[*Fert. Digest*, 12 (2) (1973-74), 15]

Naphtha & Furnace Oil Prices

Government of India has announced sharp increases in the prices of naphtha, furnace oil and three other petroleum products from January 23, 1974. One kilo litre of furnace oil will now cost Rs. 232 more than the existing price of Rs. 279.89. Naphtha will be dearer by Rs. 194 per tonne over the prevailing price of Rs. 252.25 per tonne. The ex-refinery prices of 22 lube base stock are to be increased by Rs. 337 per tonne. The selling price of secondary grade lubricants has been increased by Rs. 500 per tonne. Naphtha prices were increased twice in 1973 first on June 11 by Rs. 48.12/te and then on Aug. 22 by Rs. 60.

[*Oil Commentary*, 11 (12) (1974), 4]

Compost

The Government of India proposes to set up 45 compost plants in

the country during the Fifth Plan period in order to supplement fertilizer supplies. Grant-in-aid to the extent of 33 per cent of the capital cost of the plants will be given. It is estimated that production under this plan will be 7.5 million tonnes of urban compost annually.

Gobar Gas Plants

Over 50,000 gobar gas plants are proposed to be set up in the country during the Fifth Plan. The Union Ministry of Agriculture with the village industries commission proposes to subsidize the installation cost by 25 per cent for the first 20,000 gas units in 2,000 blocks. Subsidy will entail an expenditure of Rs. 1.5 crores.

Repeat Order for FCI Catalysts from Bulgaria

A batch of the following catalysts,

developed and prepared in the Planning and Development Division FCI Ltd., Sindri, was exported to Bulgaria in 1970: LT and HT conversion catalysts, primary and secondary steam reformation catalysts. These were charged in their fertilizer plant at Vratza. Two scientists from P & D Division later visited Bulgaria for studying the performance of the above catalysts. During their discussion with the members of Chimimport, the P & D representatives learnt that the primary and secondary steam reformation catalysts and HT and LT conversion catalysts were giving very satisfactory service. The Bulgarian representatives indicated getting a further charge of primary gas reformation catalysts and the shipment has just been made.

[*Self-Reliance*, 1 (1) (1974), 13]

STATISTICS

TABLE 1—PLANNED INCREASE IN PRODUCTION IN THE DIFFERENT COAL-MINING AREAS, mil. tonnes

Coalfields	Actual Production in 1971-72	Estimated Production in 1978-79
A. COKING COAL		
1. Bengal-Bihar	16.65	32.31
B. BLENDABLE COAL		
1. Bengal-Bihar	1.46	2.10
2. Central India Coalfields	0.29	0.70
C. NON-COKING COAL		
1. Bengal-Bihar	31.50	53.07
2. Singrauli	1.30	7.30
3. Talcher	1.02	3.83
4. Korba	1.48	4.60
5. Central India Coalfields	6.82	14.65
6. Pench-Kanhan-Tawa	3.98	7.85
7. Maharashtra	2.22	5.70
8. Singareni	4.71	10.00
9. North East region and Jammu & Kashmir	0.63	1.00
TOTAL	72.06	143.11

[Chem. Indus. News, 8 (1973), 723]

TABLE 2—STATEWISE DEMAND AND SUPPLY OF COAL, mil. tonnes

State	1972-73 Demand	Supply	Shortfall	% of Unsatisfied Demand
A.P.	2.94	2.89	0.05	2
Assam	0.31	0.21	0.10	32
Bihar	21.66	17.21	4.15	21
Gujarat	3.12	2.77	0.35	11
Haryana	0.62	0.27	0.35	56
H.P.	0.06	0.01	0.05	83
Kerala	0.02	0.01	0.01	50
M.P.	8.52	8.01	0.51	6
Maharashtra	4.08	3.94	0.14	3
Mysore	0.96	0.70	0.26	27
Orissa	4.40	3.29	1.11	25
Punjab	3.21	1.76	1.45	45
Rajasthan	1.31	1.02	0.29	22
Tamil Nadu	2.37	1.35	1.02	44
U.P.	11.06	7.30	3.78	34
W. Bengal	15.38	14.91	0.47	3
TOTAL	80.02	65.85	14.37	17.9

[Chem. Indus. News, 8 (1973), 723]

TABLE 3—STATEWISE INDEX OF AVERAGE YIELD PER HECTARE OF RICE, WHEAT, JOWAR, GRAM, SUGARCANE (CANE), COTTON, TOBACCO AND DRY CHILLIES
(All-India = 100)

State	RICE				WHEAT				JOWAR				GRAM			
	Per- cent- age of area produc- tion	Per- cent- age of produc- tion	Average yield per hectare		Per- cent- age of area produc- tion	Per- cent- age of produc- tion	Average yield per hectare		Per- cent- age of area produc- tion	Per- cent- age of produc- tion	Average yield per hectare		Per- cent- age of area produc- tion	Per- cent- age of produc- tion	Average yield per hectare	
			Kg.	Index			Kg.	Index			Kg.	Index			Kg.	Index
1. Andhra Pradesh	8.7	11.2	1,404	128	0.1	neg	242	20	4.5	13.3	462	91	1.0	0.4	262	39
2. Assam	6.0	5.4	983	90	0.1	neg	602	49	...	...	...	...	neg	neg	500	75
3. Bihar	14.5	11.2	851	78	6.9	5.9	1,052	86	0.1	neg	446	88	3.1	3.2	673	101
4. Gujarat	1.3	1.0	863	79	3.0	3.5	1,423	116	7.2	4.3	304	60	0.6	0.5	609	91
5. Haryana	0.7	0.9	1,486	136	6.0	9.6	1,974	161	1.2	0.5	213	42	12.8	16.6	866	130
6. Jammu and Kashmir	0.6	1.1	1,640	150	1.2	1.2	1,145	93	...	...	...	...	neg	neg	200	30
7. Kerala	2.4	3.2	1,454	133	...	...	...	...	neg	neg	429	85	...	...	...	...
8. Madhya Pradesh	11.6	8.0	755	69	19.0	10.9	706	58	13.6	16.9	631	125	20.7	16.5	532	80
9. Maharashtra	3.7	3.6	1,083	99	5.2	2.0	485	40	33.2	30.2	460	91	5.0	2.2	292	44
10. Mysore	3.1	5.1	1,805	165	1.9	0.6	415	34	16.1	19.7	619	122	2.6	1.7	432	65
11. Orissa	11.9	11.0	1,002	92	0.1	0.1	1,306	106	0.1	0.1	763	151	0.3	0.3	592	89
12. Punjab	1.0	1.4	1,533	140	12.8	22.9	2,201	179	neg	neg	729	156	4.9	6.0	804	121
13. Rajasthan	0.3	0.2	799	73	7.7	7.1	1,132	92	6.0	4.3	361	71	17.2	17.0	661	99
14. Tamil Nadu	7.1	11.2	1,732	158	neg	neg	333	27	3.9	5.8	741	146	neg	neg	545	82
15. Uttar Pradesh	12.1	8.3	748	68	32.6	32.2	1,210	99	4.1	4.9	597	118	29.3	32.6	744	112
16. West Bengal	13.2	15.2	1,264	116	1.4	2.3	1,972	161	neg	neg	625	124	2.2	2.7	806	121
All-India	100.0	100.0	1,094	100	100.0	100.0	1,228	100	100.0	100.0	506	100	100.0	100.0	666	100

Percentage distributions and average yields per hectare are based on 3-years' average (1968-69 to 1970-71).
neg = negligible.

TABLE 3—STATEWISE INDEX OF AVERAGE YIELD PER HECTARE OF RICE, WHEAT, JOWAR, GRAM, SUGARCANE (CANE), COTTON TOBACCO AND DRY CHILLIES—Contd.
(All-India=100)

State	SUGARCANE (CANE)				COTTON				TOBACCO				DRY CHILLIES			
	Per- centage distri- bution of area produc- tion	Per- centage distri- bution of area produc- tion	Average yield per hectare		Per- centage distri- bution of area produc- tion	Per- centage distri- bution of area produc- tion	Average yield per hectare		Per- centage distri- bution of area produc- tion	Per- centage distri- bution of area produc- tion	Average yield per hectare		Per- centage distri- bution of area produc- tion	Per- centage distri- bution of area produc- tion	Average yield per hectare	
			Kg.	Index			Kg.	Index			Kg.	Index			Kg.	Index
1. Andhra Pradesh	2.7	3.7	74.8	153	4.2	2.2	64	55	49.2	41.6	671	84	25.8	22.7	517	88
2. Assam	1.2	1.0	40.1	82	0.2	0.1	68	58	2.1	2.0	753	95	1.3	1.4	615	105
3. Bihar	6.1	4.8	39.4	81	neg	0.1	217	186	3.2	3.8	942	119	2.8	4.4	927	158
4. Gujarat	1.4	1.4	50.2	103	21.1	30.5	169	144	18.9	27.9	1,173	148	3.3	3.4	608	104
5. Haryana	6.1	5.6	44.6	91	2.6	6.9	309	264	0.2	0.1	625	79	0.9	1.5	923	158
6. Jammu and Kashmir	0.1	neg	11.6	23.7	...	...	...	...	...	...	...	...	...	...	...	...
7. Kerala	0.3	0.4	59.0	121	0.1	0.1	167	143	0.2	0.3	1,571	198	0.5	0.6	750	128
8. Madhya Pradesh	2.3	1.2	25.6	52	9.0	5.9	77	66	0.6	0.4	519	65	5.7	2.7	275	47
9. Maharashtra	7.9	10.8	66	136	36.4	20.4	66	56	2.8	1.6	450	57	22.7	21.3	550	94
10. Mysore	3.6	6.5	88	180	13.3	6.9	61	52	9.1	5.5	480	60	15.2	7.9	305	52
11. Orissa	1.4	1.5	53.9	110	...	...	...	...	3.0	3.1	813	102	4.0	3.7	544	93
12. Punjab	5.4	4.3	38.4	79	5.2	15.8	357	305	...	...	...	...	2.0	3.0	876	150
13. Rajasthan	1.6	0.6	19.2	39	3.1	3.5	130	111	1.1	1.0	708	89	3.7	3.8	602	103
14. Tamil Nadu	5.6	8.9	77.8	159	4.1	6.7	192	164	3.5	6.5	1,458	183	8.2	19.6	1,393	238
15. Uttar Pradesh	49.7	43.0	42.3	87	0.7	0.9	154	132	2.7	2.9	863	109	2.4	1.4	333	57
16. West Bengal	1.1	1.1	46.2	95	...	...	...	...	2.9	3.0	133	105	1.1	1.7	885	151
All-India	100.0	100.0	43.9	100	...	...	117	100	...	...	795	100	...	...	586	100

[Distribution of Agricultural Income in India, 1960-61 and 1970-71, (Published by Economic and Scientific Research Foundation, New Delhi-1), 1973, 28].

TABLE 4—STATEWISE DISTRIBUTION OF (1) GROSS CROPPED AREA, (2) GROSS AND NET VALUES OF AGRICULTURAL OUTPUT PER HECTARE OF NET AREA SOWN AND (3) GROSS AND NET VALUES OF AGRICULTURAL OUTPUT

(1960-61 and 1970-71)

1.—Gross Cropped Area				2.—Gross and Net Values of Agricultural Output per Hectare of Net Area Sown				3.—Gross and Net Value of Agricultural Output per Hectare of Gross Cropped Area						
State	1960-61		1970-71		Net area sown ('000 hectares)		Gross Output (Rs.) per hectare		Net Output (Rs.) per hectare		Gross Output (Rs.) per hectare		Net Output (Rs.) per hectare	
	'000 hectares	Percentage distribution	'000 hectares	Percentage distribution	1960-61	1970-71	1960-61	1970-71	1960-61	1970-71	1960-61	1970-71	1960-61	1970-71
1	2	3	4		5	6	7	8	9	10	11	12	13	14
1. Andhra Pradesh	11838	7.6	12878	7.7	1,08,05 (8.0)	1,12,76 (7.9)	518.2 (103)	1,124.5 (95)	433.1 (101)	900.1 (91)	473.1 (107)	984.8 (98)	395.1 (105)	788.4 (94)
2. Assam	2509	1.6	2921	1.7	21,33 (1.6)	23,74 (1.7)	970.5 (192)	1,975.6 (167)	923.6 (215)	1,866.0 (188)	824.1 (187)	1,604.7 (160)	783.9 (209)	1,195.0 (142)
3. Bihar	11120	7.2	10880	6.5	80,42 (5.9)	82,56 (5.8)	682.7 (135)	1,371.1 (116)	598.1 (139)	1,195.5 (121)	494.0 (112)	1,040.6 (104)	432.1 (115)	907.2 (108)
4. Gujarat	9763	6.3	9954	5.9	93,93 (6.9)	93,73 (6.6)	363.0 (72)	1,121.9 (95)	315.1 (73)	955.5 (96)	349.4 (79)	1,056.7 (105)	303.0 (81)	900.4 (107)
5. Haryana	4616	3.0	4 09	2.9	34,57 (2.6)	34,53 (2.4)	45.13 (89)	1,494.4 (126)	384.7 (89)	1,245.3 (126)	338.5 (77)	1,073.9 (107)	288.0 (77)	894.3 (106)
6. Jammu and Kashmir	804	0.5	897	0.6	653 (0.5)	7,27 (0.5)	658.3 (130)	1,609.4 (136)	551.3 (128)	1,361.8 (138)	529.7 (120)	1,229.8 (130)	448.9 (120)	1,103.1 (131)
7. Kerala	2170	1.4	2652	1.6	17,78 (1.3)	19,70 (1.4)	1,507.3 (298)	3,624.41 (307)	1,249.8 (314)	3,177.7 (321)	1,232.9 (280)	2,692.2 (268)	1,107.7 (295)	2,361.3 (281)
8. Madhya Pradesh	18242	11.7	20390	12.2	1,61,48 (11.9)	1,83,74 (12.9)	351.7 (70)	705.3 (60)	300.3 (70)	596.0 (60)	311.3 (71)	635.4 (63)	266.1 (71)	537.2 (64)
9. Maharashtra	18842	12.1	19262	11.5	78,97 (13.2)	1,82,98 (12.9)	393.9 (78)	682.0 (58)	342.0 (80)	581.5 (9)	374.2 (85)	648.1 (65)	324.7 (87)	552.5 (66)
10. Mysore	10594	6.8	10392	6.2	1,02,35 (7.6)	98,18 (6.9)	385.9 (76)	1,069.5 (90)	315.6 (73)	870.8 (88)	372.8 (85)	1,010.0 (101)	305.0 (81)	822.4 (98)
11. Orissa	6456	4.2	7796	4.7	59,79 (4.4)	56,68 (4.0)	518.5 (103)	1,448.5 (123)	461.6 (107)	1,275.6 (19)	480.6 (109)	1,052.8 (105)	426.8 (114)	927.3 (110)
12. Punjab	4661	3.0	5485	3.3	37,01 (2.7)	40,17 (2.8)	599.8 (119)	1,994.0 (169)	510.7 (119)	1,605.7 (162)	475.3 (108)	1,461.3 (146)	405.8 (108)	1,176.3 (140)
13. Rajasthan	14070	9.1	15975	9.5	1,31,66 (9.7)	1,46,63 (10.3)	246.8 (49)	667.7 (56)	205.8 (48)	554.5 (56)	231.0 (52)	612.6 (61)	192.5 (51)	509.1 (61)
14. Tamil Nadu	7137	4.6	1400	4.4	58,47 (4.3)	62,71 (4.4)	851.7 (169)	1,926.3 (163)	668.7 (156)	1,499.0 (151)	697.3 (158)	1,633.1 (163)	548.4 (146)	1,270.8 (151)
15. Uttar Pradesh	24925	16.0	26889	16.1	1,97,14 (14.6)	2,05,48 (14.5)	584.4 (116)	1,354.9 (11)	479.4 (111)	1,101.8 (111)	462.1 (105)	1,035.6 (103)	379.2 (101)	841.5 (100)
16. West Bengal	6371	4.1	7335	4.3	54,51 (4.0)	56,33 (4.0)	991.6 (176)	1,956.3 (165)	790.7 (184)	1,716.7 (173)	763.1 (173)	1,544.1 (154)	676.4 (180)	1,354.6 (161)
All-India	155371	100.0	167431	100.0	13,54,59 (100.0)	14,20,95 (100.0)	505.2 (100)	1,182.4 (100)	430.0 (100)	990.2 (100)	440.5 (100)	1,003.5 (100)	374.9 (100)	840.4 (100)

Figures in brackets in cols. 5 and 6 show the percentage distribution. Those in cols 7 to 10 the respective index nos. with all-India as 100; figures in brackets in cols. 11, 12, 13 and 14 show the indices of different items (with All-India=100).

[Distribution of Agricultural Income in India, 1960-61 and 1970-71 (Published by Economic and Scientific Research Foundation, New Delhi-1), 1973, 21, 22 and 24].

TABLE 5—WORLD POTASH DEMAND

Region	('000 tonnes K ₂ O ₃)			
	1972-73	1979-80	Growth, 1973-80	
			Tonnage	Per cent per year
Western Europe	6,260	7,620	1,360	3
E. Europe & USSR	5,990	9,980	3,990	8
U.S. & Canada	810	6,800	1,990	5
Latin America	770	1,540	770	10
Africa	280	640	360	12
Asia	1,520	2,770	1,250	9
Oceania	270	450	180	8
Total	19,900	29,800	9,900	6

[R. E. Hatch, CANPOTEX LTD., Toronto *Paper Read at FAI Seminar on World Fertilizer Situation in the Seventies* held at New Delhi, December 14-15, 1973]

TABLE 6—WORLD PRODUCTION OF POTASH

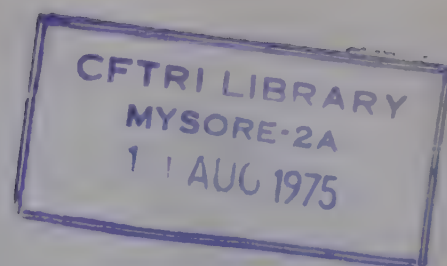
Producer	1972-73	Per cent
	Estimated Production ('000 tonnes K ₂ O 1972-73 FY)	of Total
Canada	3,820	19
United States	2,390	12
Western Europe, Congo and Israel	5,680	29
Russia and East Germany	7,860	40
Total	19,750	100

[R. E. Hatch, CANPOTEX LTD., Toronto, *Paper Read at FAI Seminar on World Fertilizer Situation in the Seventies* held at New Delhi, December 14-15, 1973].

TABLE 7—CAPACITY, PRODUCTION, OPERATING RATES OF POTASH INDUSTRY

Producer	('000 tonnes K ₂ O; 1972/73FY)		
	Production capacity	Estimated Production	Operating rate (per cent)
United States	2,700	2,390	88
Canada	7,550	3,820	51
Western Europe, Congo and Israel	6,430	5,680	88
Communist producers	7,960	7,860	99
Total	24,640	19,750	80

[R. E. Hatch, CANPOTEX LTD., Toronto, *Paper Read at FAI Seminar on World Fertilizer Situation in the Seventies* held at New Delhi, December 14-15, 1973].



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The opinions expressed by the authors are their own and do not necessarily reflect the views of the Planning and Development Division of the Fertilizer Corporation of India Ltd.

In the present study, the coefficients of friction of TSP on the steel and concrete surfaces have been determined by an apparatus fabricated in this laboratory. Variation in the particle size distribution in TSP is shown to cause significant changes in the coefficient of friction. Moisture and free phosphoric acid also affect the coefficient of friction. The results have been explained.

Rheology of Fertilizers: Friction of Triple Superphosphate Particles on Steel and Concrete Surfaces

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The rheological characteristics of bulk materials, viz. angle of repose, coefficient of friction of the particles on the sliding surfaces, angle of rupture, effective angle of friction, etc., are important parameters in the design of bins, bunkers, silos, hoppers and other storage equipments.¹⁻⁹ The two angles which are relevant of the sliding of bulk materials in chutes and hoppers and pressure distribution on the walls of storage equipments are angle of repose and angle of friction. The angle of repose is defined as the angle of elevation of a heap of granular materials, when it just begins to slide upon itself. The angles of repose for various fertilizers have been evaluated and studied in another communication.¹⁰ The angle of friction is defined as the angle to which a particular base must be elevated before the powder begins to slide upon it. In actual flow, the resistance is met in two counts, viz. in the interparticle friction in the bulk flow and in the friction of particles at the surfaces of the wall of storage equipments, giving rise to the following angles: (i) angle of internal friction and (ii) angle of friction with the wall surfaces. The angle and coefficient of friction, involving TSP particles and steel or concrete surfaces, have been evaluated and the effect of variation in the moisture content, particle size distribution and the presence of free phosphoric acid have been studied. These data are useful as steel is a common constructional material for shallow bins, bunkers and hoppers, and reinforced concrete is frequently used for large bunkers and silos. These have been determined either by the 'tilting plate method'^{4,5,11} or by 'Jenike's shear shell'^{2,7-9}. The present method is based on the following principle³ (Fig. 1).

If a body rests on a horizontal surface and force P_n represents the total vertical load on the body, which

includes the weight of the body also, the reaction to P_n is force P_r . These vertical forces make available a frictional force P_f , which comes into action to resist an applied horizontal shearing force P_s and when P_s equals P_f the body is in limiting equilibrium. If the value of P_s is increased a little beyond this, the equilibrium is disturbed and the body starts slipping. At limiting equilibrium

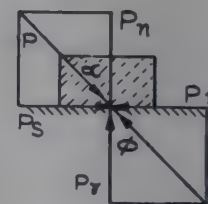


Fig 1—Friction and Criterion of Slip

$\alpha = 0$ — No Friction

$\alpha < \phi$ — Partial Friction No Slip

$\alpha = \phi$ — Full Friction Failure or Slip to Right

$\alpha =$ Angle of Obliquity of Force P due to P_s

$$P_f = P_n \tan \phi \dots\dots\dots (1)$$

where ϕ = angle of friction. This angle is related to the coefficient of friction, μ , by

$$\mu = \tan \phi \dots\dots\dots (2)$$

$$\text{or } \mu = P_f/P_n = P_s/P_n \dots\dots\dots (3)$$

ϕ and μ are properties of the materials which are in contact. The frictional resistances are influenced by the physical and chemical nature of the sliding surfaces, e.g. size, size distribution, porosity or bulk density and shape of particles, and specific surface area, hardness, roughness, etc., of the particles and the sliding surfaces.

Experimental

Description of the Apparatus: The test apparatus (Fig. 2) consists of (1) a hollow cubical container of

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transparent perspex sheet, fabricated in the laboratory, for keeping the test samples, (2) a horizontal cover with raised square face fitting properly in the container with a little clearance all-around, (3) a brass pulley fitted in a frame, (4) a pan, (5) horizontally levelled rectangular surfaces of steel and concrete and (6) arrangements for applying normal (vertical) and shearing loads. The container, having four side walls, is open at both ends, top and bottom. The thickness of the walls is 1 cm. and these walls were joined together tightly by araldite and fixing screws. The inside dimensions of the container are 6 cm. $\times$ 6 cm. $\times$ 6 cm. Near the bottom end and at the middle of one of the side walls, a hook is fitted for tying a chord passing through the pulley. The cover is made of a steel plate of size 12 cm. $\times$ 12 cm. and thickness 8 mm. with a square hole (6 cm. $\times$ 6 cm.) at the centre, where another piece of a thick steel plate of about 6 cm. $\times$ 6 cm. and thickness 40 mm. is welded, making one side of the cover raised at the centre, which can be inserted in the container as its dimensions all-around are slightly less than the internal dimension of the container. The raised face of the cover can rest at the top of the sample kept in the container. The cover serves as a platform for keeping the normal loads which are applied on the material. The pulley is fitted in such a position through which shear loads are applied by placing weights on a hanging pan tied by a nylon chord passing through the pulley. The other end of the chord

is attached to the hook in the container. All the parts detailed above are able to bear a load more than 20 kg. without any distortion or bending.

Fertilizer Samples: Powders of TSP with different moisture contents were prepared by exposing it to a constant humidity for different periods of time to enable the samples to pick up the required amount of moisture, and these samples were kept in stoppered bottles for a day or two for uniform moisture distribution. Another portion of TSP powder was agglomerated and granules were sieved into three different size gradings, viz. $-5 + 8$, $-8 + 16$ and $-16 + 44$ mesh (BSS). Granules, thus made, were however of irregular shape. Free phosphoric acid to the extent of 4 per cent was added to the TSP (containing < 0.1 per cent free acid) powder and granules, $-8 + 16$ mesh, were made as stated earlier.

Wall Materials: A steel plate of dimensions 55 cm. $\times$ 15 cm. which has been cut from an original 8 mm. thick steel plate as casted in the steel industry was used for the study. The surface was of medium finish. A concrete slab of the size 55 cm. $\times$ 15 cm. $\times$ 4 cm. was casted in the laboratory, whose top surface was made perfectly horizontal.

Test Procedure: The wall surface (steel or concrete) was placed on a frame in horizontal position. The horizontability of the surface was very carefully checked by a spirit level. For the experiments, three different positions were chosen throughout the length of the wall which acted as a plane of shearing surface. The hollow container was placed at one of its positions, and it was filled with the TSP sample. The top surface was pressed by hand and levelled. The cover was kept over the top of the container with its raised face pressing the samples inside the frame of the container without touching the side walls. Known loads were kept on the cover and shearing loads in increasing order were kept, slowly and steadily without any impact action on the hanging pan tied with the nylon chord, passing through the pulley and the hook in the container, until it was just sufficient for the slip to occur. The normal loads, including the weight of the cover and the samples and shear loads, including the weight of the pan, just sufficient to disturb the equilibrium were recorded.

To correct for the effect of friction caused by the container ends in contact with the wall surface, thread and the pulley, a blank test was made and this load was subtracted from the shear loads. To obtain an average and representative data, this procedure was

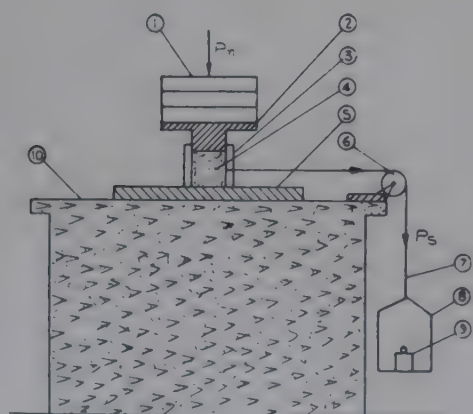


Fig 2—Experimental Set-up

Legend

1. Normal Loads
2. Cover
3. Container
4. Fertilizer Samples
5. Wall Surface
6. Pulley Fitted in Frame
7. Nylon Chords
8. Pan
9. Weights
10. Base Frame

repeated thrice for one normal load in each position, thus obtaining an average of 9 readings for the three positions of the wall surface. Each time, the wall surface was cleaned and freed from adhering samples using hair brush and duster. Rusts, if formed, on the steel surface were removed by fine emery paper, hair brush and duster so that the nature of the wall surface does not change. Since shearing strength of bulk materials increases on prolonged compaction, fresh samples were taken each time. The normal loads from about 4 to 16 kg. were applied in an increasing order of about 1 kg. giving various normal stresses on the materials in the range 0.10 to 0.45 kg./cm.². From these two values, viz. normal loads and the corresponding shear loads, the coefficients of friction or the angle of friction have been evaluated, using equations 2 and 3 for each sample and the corresponding wall surfaces.

Results & Discussion

One of the precautions taken was to include only those samples which have adequate free-flowing characteristics. This was essential, as the lumpy or highly cohesive samples gave erratic results. The variation of shearing loads in the different readings for the same sample and for a constant normal load of 4-16 kg. was of the order of 200-400 g. only. Thus, the deviations in the individual reading did not have significant effect on the coefficient of friction. The average values of the coefficient of friction were plotted at various normal loads (Figs. 3-5). The effect of wall surfaces (steel and concrete) moisture content, particles size distribution, and the presence of free phosphoric acid in TSP on the coefficient or angle of friction are discussed as follows.

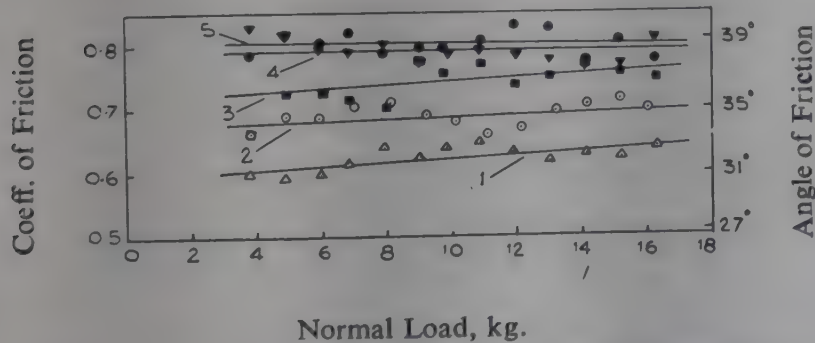


Fig. 3—Effect of Moisture on the Coefficient of Friction of TSP Powder [–16+44 mesh (BSS)]

Legend	
Test on Steel	Moisture in TSP, %
1	1.24
2	7.80
Test on Concrete	
3	1.23
4	7.80
5	8.70

The coefficients of friction of TSP powders (size –16+44 mesh), having different moisture contents, on concrete and steel surfaces at different normal loads have been evaluated (Fig. 3). It shows clearly that the coefficient is always greater on concrete than on steel surfaces. This is understandable as the roughness index of concrete surface is more than that of steel and this factor is shown to be of great importance in the following relationship given by Pilpel⁵.

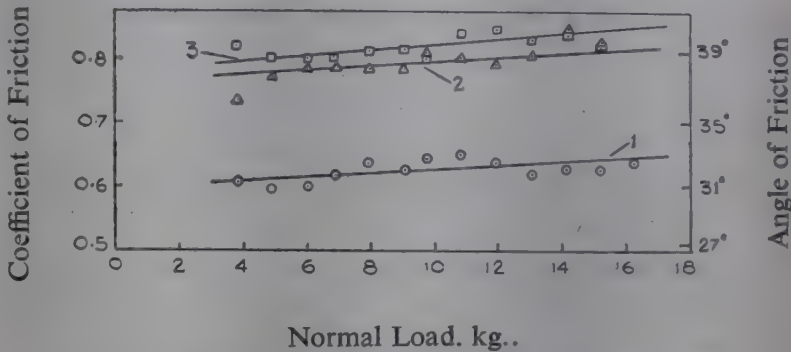


Fig 4—Effect of Particle Size Distribution on the Coefficient of Friction of TSP on Steel

Curve	Moisture, %	Size Grading, mesh (BSS)
1	1.24	– 16 + 44
2	1.88	– 8 + 16
3	1.85	– 5 + 8

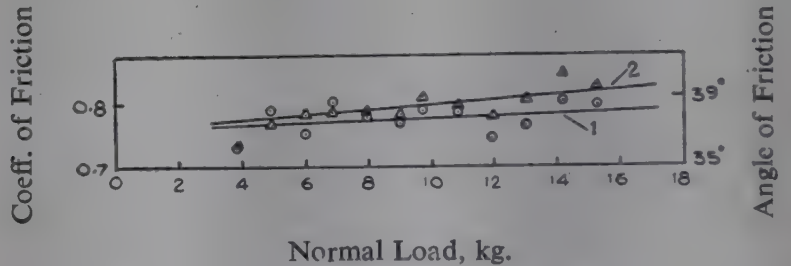


Fig 5—Effect of Phosphoric Acid on the Coefficient of Friction of TSP [–8+16 mesh (BSS); moisture 1-2] on steel

Curve	Free H ₃ P ₄ %
1.	<0.1
2.	4.0

$\tan \phi = 0.2110/Z^2 + 0.3436 (\epsilon/d)^{0.5} - 0.0171 \rho + 0.1834$, where Z = shape factor, α = particles diameter, ρ = sp. gr. of the sliding material and ϵ = roughness index of sliding surfaces. Other factors that affect the coefficient of friction ($\tan \phi$) depend on the characteristics of TSP, viz. the shape factor, the particle diameter and specific gravity, which are obviously const and $\tan \phi$ increases with the increase in the nature of the roughness factor of sliding surface. Normally TSP may contain upto 8 per cent moisture without apparently losing its free-flowing characteristics. The results, however, indicate that with an increase in the moisture content, the value of apparent cohesion increases and hence the increase in the coefficient of friction. The coefficient of friction of TSP of three

size gradings, viz. $-5 + 8$, $-8 + 16$ and $-16 + 44$ mesh, on the steel surface is presented in Fig. 4. The results show that the coefficient increases with increase in particle size. This may be attributed to the increasing irregularity in shape or the surface of the large particles. The increase in the coefficient of friction as a result of shape factor may be of a greater significance than any increase in the coefficient of friction due to the increase in area of contact when smaller particles are involved. With free phosphoric acid present to the extent of 4 per cent, it has been observed that soft lump formation occurs on increasing compaction of the sample and the slip is not sharp. The optimum shearing load is obtained with difficulty. Fertilizers adhere on the steel surface and considerable deviation in the individual values of coefficient of friction was observed though the average values remained essentially unaffected. This may be indicative of 'floodable flow'. Moreover, there is a lesser increase in the coefficient of friction at high normal loads in sample containing 4 per cent phosphoric acid, when compared to samples of same size grading with only traces of phosphoric acid (Fig. 5). As the graphs indicate that in all cases there is a tendency of increase in the coefficient of friction with increasing normal loads. This may be due to the fact that the TSP samples become more cohesive and its characteristics with respect to the surface of contact changes. The increase in shearing load is therefore, proportionately more with an increase in the normal load. Thus, the increase in coefficient of friction occurs with the increase

in normal loads. The deviation is significant on steel surface than on the concrete, possibly due to the greater affinity of liquid phase for steel.

The present study, thus, provides the data and highlights the basic differences that arise in the values of coefficient of friction of TSP particles as the nature of contact surface changes from steel to concrete. The observed increase in the coefficient of friction with an increase in the particles size of TSP is attributed to its shape factor. The influence of free phosphoric acid and moisture on the values of coefficient of friction particularly for steel surfaces are noteworthy. Further investigations are in progress.

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The effect of crystallite size on efficiency of naphtha-steam reforming and carbon liberation characteristics and the phase composition at various stages of catalyst bed life and reducibility of nickel oxide have been investigated. Three catalysts were prepared by precipitation and impregnation, out of which two comprise of alumina and nickel oxide only while the third contains calcium oxide in addition to these two oxides. In both precipitated and impregnated catalysts, nickel was present as nickel oxide, whereas the calcium-bearing catalyst contained nickel as spinel (NiAl_2O_4). It has been observed that it is more difficult to reduce a precipitated catalyst than the impregnated one. The presence of calcium makes the third catalyst more resistant to reduction. The growth of nickel crystallite is faster when the reduction is easier. In freshly reduced catalyst, the size of nickel crystallite lies in the range 164-261 Å, tending to grow in size with time. In the cases of the precipitated and impregnated catalysts, the increase in crystallite size in 30 hours is 3 and 6 times the original sizes respectively. The presence of calcium-bearing phase prevents their growth. This behaviour appears to have a direct bearing on conversion efficiency of the catalysts. In the calcium-bearing catalyst where crystallite growth is arrested, the fall in conversion with time is negligible. The extent of carbon laydown also appears to be related with crystallite size growth; minimum carbon deposit is associated with least increase in crystallite size.

Naphtha-Steam Reformation Catalyst—Effect of Physical Parameters on Activity and Carbon Deposition Intensity

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Naphtha-steam reforming reaction is associated with side reactions, like hydrocracking, polymerization, resulting in carbon deposition leading to a fall in the activity level of the catalyst. Incorporation of alkali and alkaline-earth oxides in the catalyst is a popular practice which helps to retain catalyst activity either by suppressing the undesirable side reactions or by accelerating the carbon gasification rate. But the alkali appears to have disadvantages too due its volatility at the reforming condition¹⁻². The resultant multicomponent system reduces acidity³ of the catalyst and thus takes care of carbon by accelerating its gasification rate.

For a good reforming catalyst, in general, attempts were made for selecting such a support which will be thermally stable and offers a large surface to affect fine dispersion of the catalytic components. However, in naphtha-steam reforming high reaction temperature and environment are conducive to the growth of the active metal crystallites. It is found that most of the catalysts at the initial stage undergo trouble-free operation. But it is only with the time of operation that carbon formation gets accelerated. It, therefore, seems reasonable to study whether there is any relationship between

the growth of nickel crystallite and carbon deposition under the operating conditions of the reformers.

In this connection, reference may be made to the work of Dorling *et al*⁴, who had observed that activity of supported catalyst deteriorates with growth of crystallite size. The evidence of the effect of crystallite size on hydrogenolysis and isomerisation has been cited in literature⁵⁻⁷. Similar investigation in the field of naphtha-reforming catalyst may be helpful to correlate the performance with its physical parameters.

The present investigation deals with the influence of crystallite size on carbon liberation characteristics as well as on efficiency of naphtha-steam reforming. The role of physical parameters of the carrier on crystal growth has also been included in this study. In addition, this paper deals with the reducibility of the active component with particular reference to physical and chemical parameters of the catalyst as a whole and the resultant effect of carbon liberation intensity.

Experimental

For the present investigation, three catalysts, designated as A, B and C with identical nickel content (10

per cent), were taken. The active component was incorporated in the α -alumina support, following different techniques. The catalyst C contained lime in addition to alumina and nickel.

Catalyst A: Prepared by precipitation of nickel from nickel nitrate (98 per cent purity) on alumina by ammonium carbonate solution.

Catalyst B: Prepared by impregnation of alumina in nickel nitrate solution.

Catalyst C: Similar to sample A but calcium is incorporated by impregnation in calcium nitrate (98 per cent purity) solution.

Subsequently, all the samples were finally heated at 800°C for 8 hr. to decompose the salts.

The catalysts were tested in a bench scale reactor (Fig. 1) of 24 mm. I.D. and 500 mm. length. About 70 cc. of 1.5–2.0 mm. size catalyst granules were packed in the reactor on a perforated S/S disc. Naphtha and water were passed through the preheating section using separate rotameters.

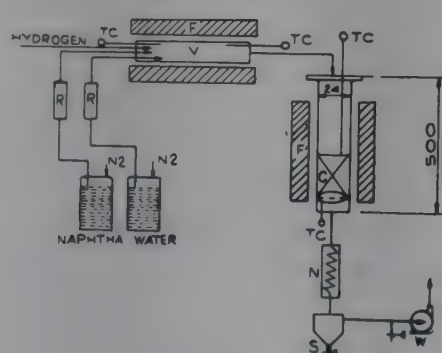


Fig 1

The naphtha vapour and steam got mixed in the pre-heater and then entered into the reactor tube. The required temperature was maintained by controlling the power input to the furnace. The thermocouples placed at the top and bottom of the reactor measured the gas temperature. During activity measurement, the steam-naphtha mixture was heated to 500–520°C, before it is contacted with the catalyst bed. The reformed gas temperature at the bed exist was maintained at 800°C, and the hot gas passed through a cooling section for separation of the condensate and then metered and analysed. All experiments were conducted at atmospheric pressure.

(1) *Steaming*: The reactor was packed with catalyst, assembled and pressure-tested. After the reactor was brought to the desired temperature in a stream of

nitrogen, the catalyst was steamed for 8 hours, followed by cooling to room temperature in a stream of nitrogen.

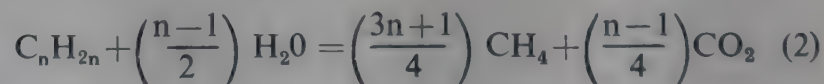
(2) *Reduction*: The effect on reducibility caused by variation in method of preparation was studied at 300° and 600°C under atmospheric pressure. The reduction was carried in a current of steam and hydrogen; the concentration of hydrogen being 10 mole per cent. The flow of the reducing mixture was discontinued after 8 hours and the catalyst cooled in presence of nitrogen. The discharged sample was kept in an inert atmosphere.

(3) *Reforming*: Experiments were carried out using all the three types of catalyst at 800°C (catalyst bed outlet) and atmospheric pressure, steam/carbon ratio equal to 4 (moles per carbon atom.) and L.H.S.V. of 0.5 (g. of naphtha/g. cat./hr.). The characteristics of naphtha feed are as follows: boiling range 40–158°C; density 0.70–0.71 g./cc.; carbon/hydrogen ratio 5.8–6.0; aromatics 14.6–16.0% wt.; olefines 0.2–0.5% wt.; saturates 83.4–85.0% wt.; mol. wt. 97 ± 1 ; and sulphur 0.5 ppm.

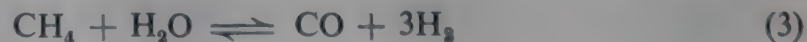
The catalyst sample was first reduced at 600°C for 8 hours and then the temperature was raised to 800°C. In the case of catalyst C, reduction was affected at 800°C. Superheated steam and naphtha vapour along with hydrogen (hydrogen-to-naphtha molar ratio 0.5) allowed to flow through the catalyst bed. After specific intervals of time, the gas sample was collected for analysis. The hydrocarbon conversion was calculated on the basis of the following equation.

$$\text{Per cent Conversion} = \frac{P_{\text{CO}} + P_{\text{CO}_2}}{P_{\text{CO}} + P_{\text{CO}_2} + P_{\text{CH}_4}} \times 100 \quad (1)$$

The theoretical conversion of 99.93 per cent at the above experimental condition was calculated on the basis of equation given by Dent⁹.



where n is usually taken as 7 for light naphtha. The methane formed by the above reaction then undergoes reversible reactions with steam in the following way.



The theoretical gas composition was calculated at reactor exit temperature and the percentage conversion calculated on the basis of theoretical gas composition. For estimating the carbon deposited on the catalysts after completion of the performance test, the bed was cooled down in an inert atmosphere.

The reforming activity was also investigated with the same catalysts reduced at 300°C. The per cent methane slip for the catalyst samples A, B and C are 2.0, 2.4 and 3.0 respectively. The pressure drop across the bed increased considerably after 8-10 hours of run due to formation of carbon and dust (Table 3).

X-ray photographs of all the catalyst samples fresh, steamed, reduced and discharged after reforming reaction were taken in a Guinier camera using $\text{CuK}\alpha$ radiation, x-ray tube running at 40 KV and 20 mA. The d-spacings were calculated accurately and the phase identification was done by the method of Hanawalt *et al.*⁹

The particle size of nickel present in the catalyst samples which were discharged after a specific interval of time were determined by line broadening method using the Scherer formulation.

$$B = \frac{0.9 \lambda}{t \cos \theta},$$

where B = broadening of diffraction line measures at half its maximum intensity (radians).

θ = Bragg angle of the diffraction line of the test sample.

t = crystallite size, Å

λ = wave length of the x radiation, Å

Results and Discussion

It is known that the size of the reduced metal crystallites and their growth with aging depends on the process of activation and nature of its distribution on the support material. When the degree of interaction is less intense and the active metal is present in a massive form, where the interaction of nickel with the support is negligible, the reduction is faster but at the same time due to proximity of the reduced metal atoms, the growth of the crystallite becomes fast. It has been observed that in the present investigation the reducibility of nickel oxide depends on the method of its incorporation in the support. The growth of the crystallites is faster where the reduction is easier. There is evidence that reducibility of the supported nickel catalysts, prepared according to different methods, varies widely. The reoxidation of the reduced catalysts, which occurs in presence of steam at 700-800°C in commercial reformers in a steam cycle during shut down periods, may modify nickel oxide in such a manner that its subsequent reduction proceeds at a faster rate. This lends support to the view that nickel oxide may be present in the catalyst in different states of energy level.

The results of the present investigation appear to show that the size of the nickel crystallites and their relative growth have influence on activity, selectivity and stability of a reforming catalysts.

(a) *Phase Composition, Process of Activation and Reducibility of the Catalysts:* The phase compositions of the three catalysts in the different stages of activation and reaction have been investigated by x-ray diffraction, which showed that the fresh catalysts A and B consist of α -alumina and nickel oxide (NiO) as principal components. The catalyst C comprises oxides of alumina, nickel and calcium, and a major fraction of nickel is present in combination with alumina as spinel (NiAl_2O_4). Free nickel oxide is present in traces. Presence of free lime could not be detected. Calcium oxide is present in combination with alumina as $\text{Ca}(\text{AlO}_2)_2$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$.

In the process of activation all the three catalysts were exposed to steam for about 8 hours, when the bed was kept at 300 and 600°C separately. It may be seen from the x-ray results that steaming at 300°C does not bring any change in the phase composition except in the case of catalyst B. It is interesting to note that catalyst B at 300°C in a steam atmosphere showed appearance of γ -alumina and again showed sign of change in phase composition at 600°C, whereas the other two varieties, viz. A and C, retained their original states. At 600°C appearance of NiAl_2O_4 and elimination of γ -alumina in catalyst B is very significant. It appears that γ -form of alumina which appeared at 300°C reacted with nickel oxide (NiO) at higher temperature to account for the appearance of nickel aluminate.

The results with catalyst B (Table 1) also indicates that reducing atmosphere inhibits the formation of spinel (NiAl_2O_4). This phase did not show its existence either at 300 or 600°C in a reducing environment. It is further observed that with this catalyst even at 300°C there is appearance of nickel phase. The other catalysts, however, did not show any sign of reduction at this temperature. The reducing atmosphere revealed certain interesting features of the catalyst C also. It can be seen that phase $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$, which was present in the original catalyst and persisted in a steam environment at 300 and 600°C, disappeared under a reducing atmosphere allowing it to be completely replaced by calcium aluminate [$\text{Ca}(\text{AlO}_2)_2$] at both these temperatures. It can, therefore, be said that the reducing atmosphere affects the stability of $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$. Incidentally, the change-over of this phase to calcium

TABLE 1—CRYSTALLINE PHASES PRESENT IN THREE CATALYST SAMPLES

Experiment	Catalyst A	Catalyst B	Catalyst C
Fresh sample	α -Al ₂ O ₃ , δ -Al ₂ O ₃ , K-Al ₂ O ₃ , NiO	α -Al ₂ O ₃ , NiO, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca ₃ Al ₁₀ O ₁₈ , Ca(AlO ₂) ₂ , δ -Al ₂ O ₃ , NiO
Steamed at 300°C	α -Al ₂ O ₃ , δ -Al ₂ O ₃ , K-Al ₂ O ₃ , NiO	α -Al ₂ O ₃ , NiO, δ -Al ₂ O ₃ , K-Al ₂ O ₃ , γ -Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca ₃ Al ₁₀ O ₁₈ , Ca(AlO ₂) ₂ , δ -Al ₂ O ₃ , NiO
Steamed at 600°C	α -Al ₂ O ₃ , δ -Al ₂ O ₃ , K-Al ₂ O ₃ , NiO	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄ , δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca ₃ Al ₁₀ O ₁₈ , Ca(AlO ₂) ₂ , δ -Al ₂ O ₃ , NiO
Reduced at 300°C	α -Al ₂ O ₃ , δ -Al ₂ O ₃ , K-Al ₂ O ₃ , NiO	α -Al ₂ O ₃ , NiO, δ -Al ₂ O ₃ , K-Al ₂ O ₃ , Ni, γ -Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca(AlO ₂) ₂ , δ -Al ₂ O ₃
Reduced at 600°C	α -Al ₂ O ₃ , δ -Al ₂ O ₃ , Ni, K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, NiO, δ -Al ₂ O ₃ , K-Al ₂ O ₃ , γ -Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca(AlO ₂) ₂ , δ -Al ₂ O ₃
Reduced at 800°C	—	—	α -Al ₂ O ₃ , Ni, NiAl ₂ O ₄ , Ca ₃ Al ₁₀ O ₁₈ , Ca ₃ Al ₂ O ₆
Discharged sample (reduced at 300°C) after 10 hours reforming	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ni, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ni, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca ₃ Al ₁₀ O ₁₈ , δ -Al ₂ O ₃
Discharged sample reduced at 600°C after 10 hours reforming	α -Al ₂ O ₃ , Ni, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , δ -Al ₂ O ₃ , Ni, γ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , NiAl ₂ O ₄ , Ca ₃ Al ₁₀ O ₁₈ , Ni, δ -Al ₂ O ₃
20 hours	α -Al ₂ O ₃ , Ni, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, δ -Al ₂ O ₃ , γ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, Ca ₃ Al ₁₀ O ₁₈ , δ -Al ₂ O ₃
25 hours	α -Al ₂ O ₃ , Ni, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, γ -Al ₂ O ₃ , δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, Ca ₃ Al ₁₀ O ₁₈ , δ -Al ₂ O ₃
30 hours	α -Al ₂ O ₃ , Ni, δ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, δ -Al ₂ O ₃ , γ -Al ₂ O ₃ , K-Al ₂ O ₃	α -Al ₂ O ₃ , Ni, Ca ₃ Al ₁₀ O ₁₈ , δ -Al ₂ O ₃

aluminate will account for increase in alumina phase content in the matrix.

Another interesting feature of this multi-component system is that its nickel oxide content in the original and steam-treated catalysts disappeared under reducing condition and all the nickel content assumes the form of NiAl₂O₄. Following the sequence of reduction based on appearance of nickel phase in the system, one finds catalyst C most difficult to reduce.

Of all the three catalysts studied, nickel oxide content of catalyst B only starts getting reduced at 300°C at which neither Agnor C showed any sign of reduction. Again, except for catalyst C, reduction was nearly completed at 600°C. In case of catalyst C although reducing atmosphere induced change in the Al₂O₃-CaO-NiO system, the nickel phase did not appear before 800°C. At this temperature also both nickel and NiAl₂O₄ co-exist and complete reduction takes much longer time. The overall picture thus clearly indicates the complications involved in the reduction mechanism. The temperature necessary for reduction varies from catalyst to catalyst differing in the method of preparation. The extent and the rate of reduction is thus found to be dependent on the phase composi-

tion. Introduction of lime has made the catalyst resistant to the process of reduction. The presence of NiAl₂O₄ in the catalyst may be one of the reasons for this retarding effect but that may not be the only reason because NiAl₂O₄ which appeared in steam cycle with catalyst B did not exist in the reducing atmosphere. Under these circumstances, it appears that calcium-bearing phase exerts influence on the stability of NiAl₂O₄.

The ease of reduction of nickel oxide incorporated by impregnation may be due to the fact that its major portion is deposited on the geometric surface and has little interaction with the support. Further, there is possibility of formation of 'hills' to account for its ease of reduction. Reinan and Selwood¹⁰ have reported that it is more difficult to reduce nickel oxide in co-precipitated NiO-SiO₂ than impregnated NiO-SiO₂. Vernon *et al*¹¹ made similar observation in the cases of nickel oxide alumina impregnated and co-precipitated. In the present study also the catalyst A is found more difficultly reducible than B.

In view of the fact that nickel is present in both the catalysts as nickel oxide, it can be stated that the phase

composition cannot predict reduction characteristics of a catalyst. This difference in reducibility appears to be dependent on the degree of aggregation of the nickel oxide crystallites. The one having fine distribution will tend to have interaction at the phase boundary with the carrier and thereby likely to inhibit reduction. It follows that in case of co-precipitated catalyst nickel oxide is in finer state of distribution.

In catalyst C nickel is present only as spinel and remains in an unreduced form even at 600°C. When the temperature is further increased to 800°C reduction starts. But even after 8 hours of reduction part of the nickel is still present as spinel. It may be noticed here that with the appearance of reduced nickel in NiO-Al₂O₃-CaO system, calcium aluminate phase has disappeared and the original calcium-bearing phase, viz. Ca₃Al₁₀O₁₈, and a phase Ca₃Al₂O₆ have appeared. Lime CaO and alumina ratio in Ca(AlO₂)₂, Ca₃Al₁₀O₁₈ and Ca₃Al₂O₆ are 1:1, 3:5 and 3:1. Of the two calcium compounds Ca₃Al₁₀O₁₈ and Ca₃Al₂O₆, the latter was present in traces. From the above composition, it appears that the reduction of NiAl₂O₄ to metallic nickel may be preceded by the interaction of Ca(AlO₂)₂ and NiAl₂O₄, whereby alumina is transferred from nickel aluminate phase to calcium aluminate resulting into the formation of free nickel oxide and Ca₃Al₁₀O₁₈ in which CaO:Al₂O₃ ratio is lowered. Whatever may be the mechanism of reduction, prior formation of nickel oxide in the system seems essential for reduction of nickel aluminate to metallic nickel. This assumption is further supported by the fact that when reduction of nickel aluminate is complete, calcium assumes the original phase composition Ca₃Al₁₀O₁₈.

The extent of reduction was also studied by the thermogravimetric method (Fig. 2). It is observed that at 600°C under the experimental conditions, 99.8 and 80.6 per cent nickel oxide was reduced in the cases of B and A respectively compared to 9 per cent for C.

(b) *Relation between Crystallite Size and Reducibility and Activity of Catalysts:* The results (Table 2) indicate that the state of aggregation of nickel reduced under the same condition is different for different catalysts. The size of the reduced nickel crystallites and their growth with time appear to vary depending on the phase composition and method of preparation.

According to Hill and Selwood¹² the reduced nickel atoms have no tendency to aggregate during the use of the catalysts. The tendency is for further dispersion to take place by a process of solid solutions. However, under the reforming conditions the present observations

are different. From the data presented, it can be seen that during the 30 hours run, with catalysts A and B, there is a definite trend in nickel crystallites to aggregate than disperse. Nickel crystallites in a precipitated catalyst increased their size three-fold, whereas in the case of impregnated catalyst the increase is six-fold. The operating range of temperature and process conditions were identical in both the cases. This difference in crystallite behaviour with that stated by earlier investigators may be due to the difference in the distribution of nickel on the support and severity of operational parameters. The character of the catalyst C is distinctly different from that of the other two, with respect to crystallite growth. The initial crystallite size of the reduced metal in catalyst C was 261 Å. This is comparatively larger than that of the initial sizes of other two catalysts. The initiation of reduction at a much higher temperature may be the reason. It is really interesting to find that nickel crystallites of catalyst C have no tendency to aggregate with time.

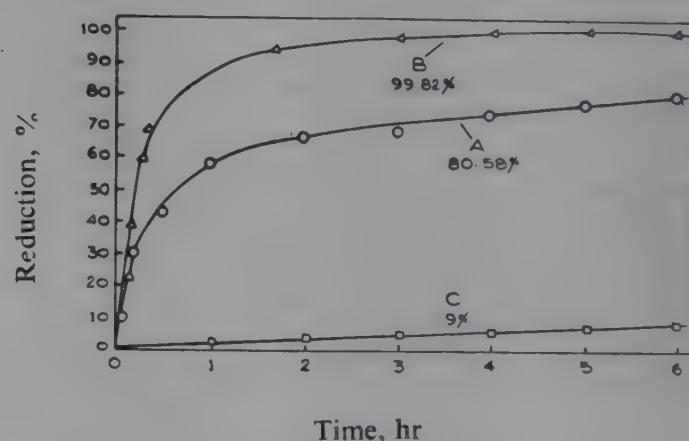


Fig. 2

TABLE 2—CRYSTALLITE SIZE (MEAN), Å

Experimental Condition	Hours of Run.	Catalyst A	Catalyst B	Catalyst C
Catalyst reduced at 300°C	8	Not measurable	—	—
Catalyst reduced at 600°C	8	302	Not measurable	—
Reforming reaction after reducing at 300°C	10	357	523	—
Reforming reaction after reduction at 600°C	10	250	164	261
	20	350	338	274
	25	442	523	269
	30	720	960	285

From the activity of the three catalysts (Table 3 and Fig. 3) it may be observed that the activity of the individual catalyst has a close relation with the crystallite

size. The initial activities of all the catalysts were almost identical. The fall in conversion level is high in case of B where the tendency of crystallite to aggregate is relatively higher. The size of the reduced nickel crystallite in catalyst C remained practically unchanged and it maintained a steady level of activity.

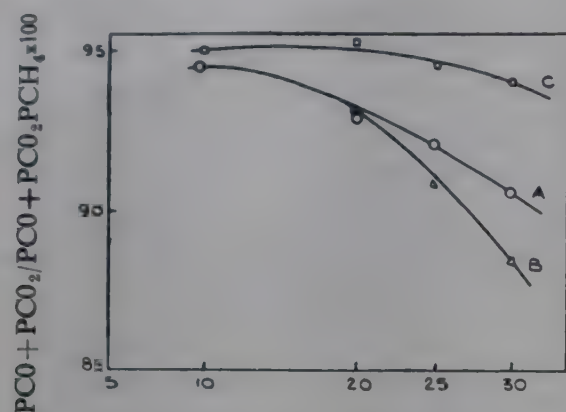


Fig. 3

TABLE 3—ACTIVITY AND STABILITY OF DIFFERENT CATALYST SAMPLE

Catalyst Sample	Period of Run, hr	% Conversion	Carbon Deposited in Discharged Catalyst (average of the bed)
<i>Reduction at 300°C</i>			
A	10	93.1	4.26
B	10	92.0	3.91
C	10	90.3	4.58
<i>Reduction at 600°C</i>			
A	10	94.5	1.10
	20	92.9	1.72
	25	92.1	3.78
	30	90.6	3.88
B	10	94.5	1.19
	20	93.1	2.21
	25	90.8	3.49
	30	88.4	3.99
C	10	95.0	1.08
	20	95.2	1.52
	25	94.6	1.88
	30	94.0	2.12

It had not been possible to measure the crystallite size when the catalysts were reduced at 300°C because of the low concentration of reduced metal in the mass.

The loss of activity accompanying crystallite growth has been reported by other authors^{4,6,13,14}. The loss of activity is stated to be caused by the loss of metal surface area due to the increased size of the crystallites. The metal area of a catalyst may be given by the rela-

tion¹⁴ $S = \frac{A}{rd}$ in (meter)²/g. where r is the edge length

of the cube in angstrom units, ' d ' is the density, and ' A ' is a constant. Obviously, metal surface area will decrease with increase in the size of the crystallites.

The rate of carbon deposition has been followed from material balance of the feed and product composition. To confirm the data the catalyst samples discharged at different intervals were analysed for deposited carbon. The calculated and analysed data compared well (Table 3). It may be observed that carbon deposition rate is higher when the catalyst is reduced at 300°C. When reduction is carried out at this temperature, the rate of coke deposition is independent of composition of the catalyst and their method of preparation. The picture is different when the catalysts are reduced at 600°C. Freshly reduced surface induces carbon liberation almost identically irrespective of its previous history. But the intensity of carbon liberation is affected to a different degree with the aging of the catalyst.

According to Voorhies¹⁵, for a given catalyst, feed-stock and temperature, the weight per cent of carbon deposited on a cracking catalyst is approximately a log function of time. The equation takes the form $C_C = At^n$. In the present study an attempt has been made to find whether this simple relationship applies in the case of carbon deposition on a steam-reforming catalyst. It has been observed that the equation applies remarkably well in the cases of catalysts B and C. The results are erratic in the case of A. The results for catalysts B and C are presented in Fig. 4. The slope of the curves may be considered as an index of carbon deposition intensity. It is apparent that the accumulation rate of carbon is minimum for C. The presence of carbon in the discharged catalysts shows that the formation of coke on the catalyst surface occurs but the carbon gasification rate is slower than that of carbon formation on the catalyst surface and the former rate is different for different catalysts. The lower value of ' n ' in the case of C shows that whatever may be mechanism of carbon lay-down, the calcium-bearing phases in the catalyst may be responsible for reduction of carbon deposition intensity.

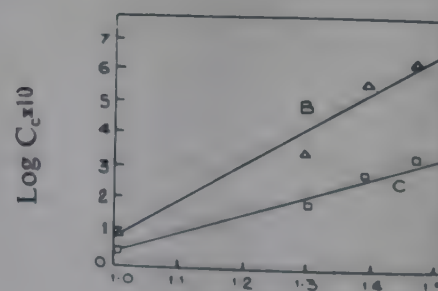


Fig. 4

Now, it may be said that lime is directly responsible in enhancing the carbon gasification rate. But the contribution of the calcium-bearing system in arresting growth of nickel crystallite and the resultant effect on reduction of carbon accumulation rate cannot be overlooked. From the data (Table 3) and the performance of industrial reformers, it is known that with aging a catalyst gets more prone to carbon liberation. Again, in most of the catalysts the crystallites grow progressively with time. Keeping this in view and considering the fact that at the initial stage the catalyst does not pose problem in industrial reformers on account of carbon deposition it is quite reasonable to assume that crystallite size may have some form of control on the rate of carbon accumulation. Therefore, arresting the tendency of crystallite growth probably can contribute to solve the carbon deposition problem. Thus, the results of the present investigation do not contradict the idea of addition of alkali or alkaline-earth to a catalyst for enhancing the rate of carbon gasification but offers alternative possibility for controlling carbon liberation by arresting the growth of nickel crystallite in naphtha-steam reforming catalyst.

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The feasibility of correlating laboratory data with commercial performance have been examined. Laboratory investigation includes measurement of structural parameters and activity test under simulated plant conditions. Reforming activity and stability of the different catalysts followed identical order in laboratory test as well as in plant performance. Higher pore volume appears to be associated with higher reforming activity but pore volume comprising of micropores may not impart good activity. Catalyst with highest surface area $53.5 \text{ m}^2/\text{g}$. shows maximum reforming activity, but there is no linear relationship between surface area, nickel content, pore diameter or particle size with activity. A catalyst containing appreciable alkali and alkaline earth oxides showed sustained reforming activity, but its mechanical strength got adversely affected while in service. For correct selection of a catalyst for industrial purpose investigation in probable change in phase composition and crystal growth under service conditions has been suggested.

Steam—Naphtha Reforming Catalyst: Application of Laboratory Data for Industrial Evaluation

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Introduction

Extensive studies¹⁻⁶ have been made on the steam-reformation of liquid hydrocarbons but seldom attempts were made to correlate the laboratory observations for commercial purpose. This may be due to the absence of sufficient laboratory data on catalysts which have proved industrially acceptable. But with the current advancement in process technology continuously demanding better reformation catalyst to work at a lower steam-to-carbon ratio, reduced exit temperature and higher throughput, it is essential to decide the norm for evaluation of catalyst in the development stages with particular reference to its suitability for commercial units.

The initial period of reformation efficiency of different varieties of commercial catalysts does not vary much. It is only with the period of operation the difference in sustained efficiency gets magnified due to change in parameters with period of operation. So initial physical, physico-chemical data and activity tests on bench scale units may not be effective for commercial evaluation of catalyst. But at the same time it is not possible to test all batches of catalysts under laboratory conditions for the entire period of expected life. Now under the above circumstances, in addition to the study of those parameters which are likely to undergo changes with the

period of operation, it is worthwhile to have a complete assessment of above parameters of catalyst before charging in a commercial unit and follow closely its behaviour in plant during its period of service.

In accordance with the above, in the present investigations attempts have been made to examine the feasibility of correlating the laboratory data with the plant performance of four varieties of commercial catalysts designated as A, B, C and D. The physico-chemical data and activity results in bench and pilot units as well as performance in commercial reformers have been studied and discussed.

Experimental

Four commercial catalysts designated as A, B, C and D were taken for the present investigation. The studies include the following aspects: (1) chemical composition, (2) porosity, pore size and, mechanical stability, and (3) activity in bench, pilot and plant scales.

Chemical Composition: Each of the four catalysts has been analysed for its chemical composition, and the results are given in Table 1. The trace elements have not been taken into consideration.

TABLE 1—CHEMICAL COMPOSITION OF THE CATALYSTS, % wt

	Catalysts			
	A	B	C	D
1. Loss on Ignition	1.0	11.1	10.2	1.4
2. Silica	—	10.2	0.5	—
3. Alumina	46.6	25.4	64.4	83.3
4. Fe ₂ O ₃	—	5.2	—	—
5. TiO ₂	22.8	—	—	—
6. Nickel as NiO	21.3	19.1	19.0	15.2
7. Lime	7.2	16.2	3.9	—
8. MgO	—	10.9	0.5	—
9. Alkali (Na ₂ O)	—	0.64	0.2	—
10. K ₂ O	—	0.95	1.60	—

TABLE 2—PHYSICAL AND MECHANICAL PROPERTIES OF THE CATALYSTS

	Catalysts			
	A	B	C	D
1. Pore Volume, cc./g. Å	0.2119	0.1488	0.2183	0.2653
2. Average Pore Diam.,	4.365	188	326	99
3. Surface Area, m ² /g.	0.95	15.8	13.45	53.5
4. Crushing Strength, kg./cm ² .	50 (Dead load)	452	466	362

Porosity, Pore Size and Mechanical Stability : Specific pore volume of the catalyst was calculated from helium and mercury displacement data. The average pore size (Table 2) was calculated from respective specific surface and porosity as follows :

$$d_p = \frac{4 V_p}{S} \times 10^4,$$

where, d_p = average pore diam., Å

V_p = p. porosity, cc.g.

S = Sp. surface area, m²/g.

Mechanical stability kg./cm.² was determined by a tensometer. For each sample crushing strength of 10-12 tablets was determined and the results computed as mean crushing strength (Table 2).

Activity Test : The activities of the catalysts have been studied in a bench scale unit (Fig. 1). There are two reservoirs (R_1 , R_2)—one for naphtha and the other for water. A calculated amount of naphtha and water was pushed under nitrogen pressure in the vaporiser (V_p). For measuring the flow suitable rotameters (RM_1 , RM_2) were used. The vaporizer was maintained at 440-450°C and both naphtha and water were pushed in the packed bed of the vaporizer in the form of jets. The required volume of hydrogen was also injected in the vaporizer from a cylinder.

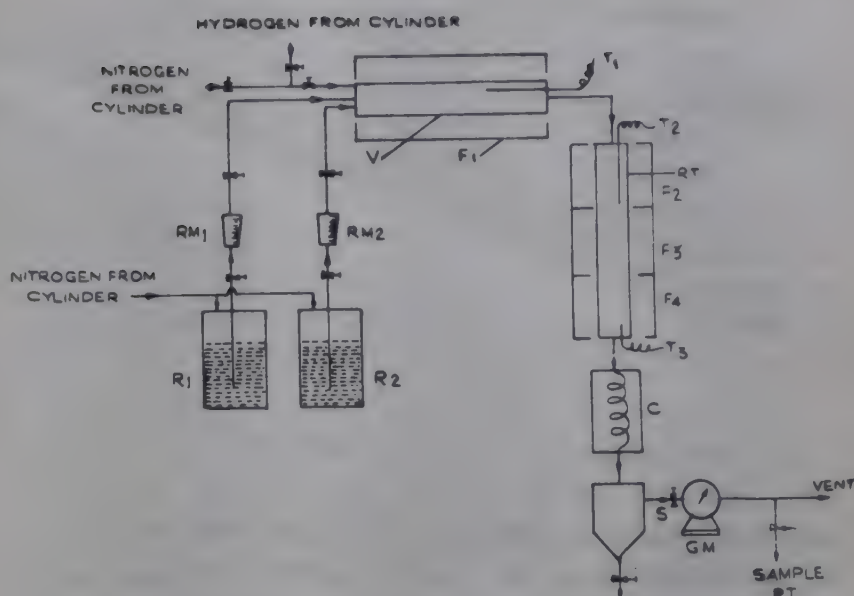


Fig. 1—Steam Naphtha Reformation Bench Scale Unit
Legend

- R_1 Naphtha Reservoir
- R_2 Water Reservoir
- RM_1 Naphtha Rotameter
- RM_2 Water Rotameter
- V Vaporizer
- RT Reactor Tube
- F_1, F_2, F_3 & F_4 —Electrical Furnaces
- T_1, T_2, T_3 —Thermocouples Connected to Temperature Recorder
- C Condenser
- S Separator
- GM Gas Meter

The reactor tube of 21 mm i.d. made from AISI 310 steel, was placed in a set of furnaces consisting of three separate units having independent control for power supply. This gave a greater flexibility for setting the different parts of the reactor to the desired temperature. The catalyst bed was housed in the middle chamber. The reformed, gas passed through the condenser (C) and separator (S) and finally released to vent.

In each experiment 60-70 g. of catalyst made into suitable size (4-5 mm.) were charged. After preheating in nitrogen stream followed by steam, the unit was charged with naphtha. Most of the experiments were conducted at 820°C, pressure 10 kg./cm.² and LHSV 0.7. The reactions were studied under steam-to-carbon ratios of 4 and 5 only. For studying the changes in mechanical strength during steaming, experiments were conducted at atmospheric pressure only. In the case of catalyst A, the LHSV 0.7 could not be used because of its low activity and consequent slippage of naphtha. In this particular case, naphtha flow was reduced to LHSV 0.35 and hydrogen flow maintained at the rate of 0.4 mole per mole of naphtha feed.

TABLE 3—CHARACTERISTICS OF NAPHTHA FEED

1. Boiling Range	40—158°C.
2. Density at 15°C	0.00— 0.71 g./c.c.
3. Total Sulphur	5— 10 ppm
4. Carbon/Hydrogen Ratio	5.8 — 6.0
5. Aromatics	15.0—16.0%
6. Olefines	1.2 — 1.5%
7. Saturates	82.4—84.0%
8. Mol. Wt.	97±2.

The desulphurized naphtha (Table 3) was used as feed and the catalysts were tested under simulated industrial plants conditions (Table 4). For determination of gas composition an average sample collected over one hour was analysed. After the completion of the experiment, naphtha was withdrawn, steam and nitrogen continued till the temperature dropped to 500°C and finally cooled in nitrogen.

In a separate set of experiments, samples B and D were studied for change in mechanical properties in presence of steam. With catalyst D, fresh sample was again charged and after activation naphtha was introduced at the rate of LHSV 0.8. The bed temperature was maintained at 820°C and reaction continued for 4, 8, 12 and 20 hours. After a specified interval of time, the sample was taken for determining the mechanical strength.

Catalysts B and D were also tested for sustained activity. They were heated in nitrogen and then in steam and finally after activation naphtha was charged at the rate of LHSV 0.8. The bed was maintained at 820°C and system pressure 10 kg./cm². The gas sample was analysed at intervals of 4, 8, 12, 16 and 30 hours.

The changes in mechanical strength of the catalysts B and D are shown in Fig. 2. Activity expressed as equilibrium constant (K_p)_(obs) calculated from wet gas composition (Figs. 3 and 4 ; Tables 4 and 5).

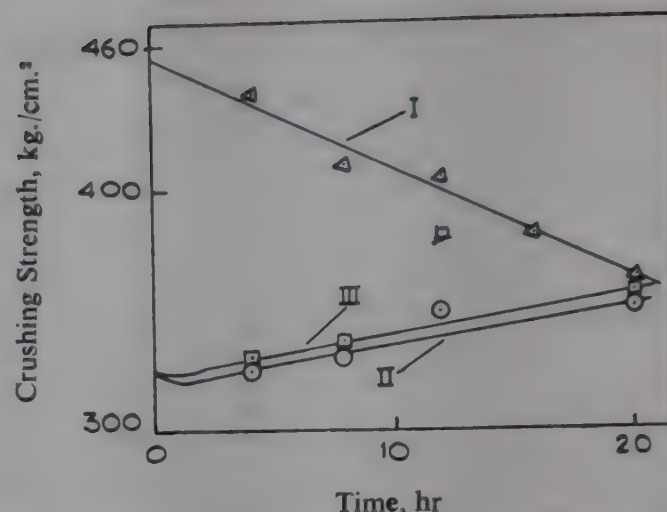


Fig. 2—Change in Crushing Strength as a Function of Time
I After Steam Treatment (Cat. B)
II After Steam Treatment (Cat. D)
III After Steam-Naphtha Treatment (Cat. D)

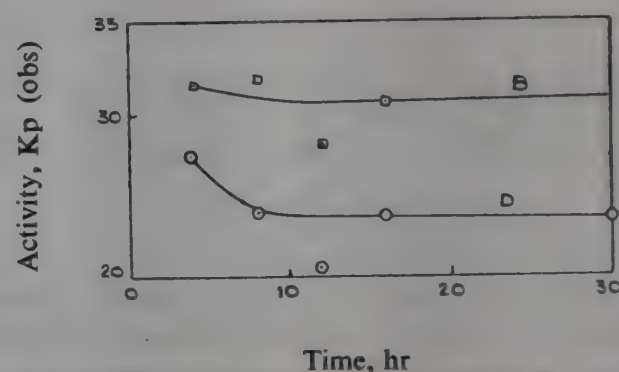


Fig. 3—Activity (K_p)(obs) as a Function of Time [Laboratory Data]

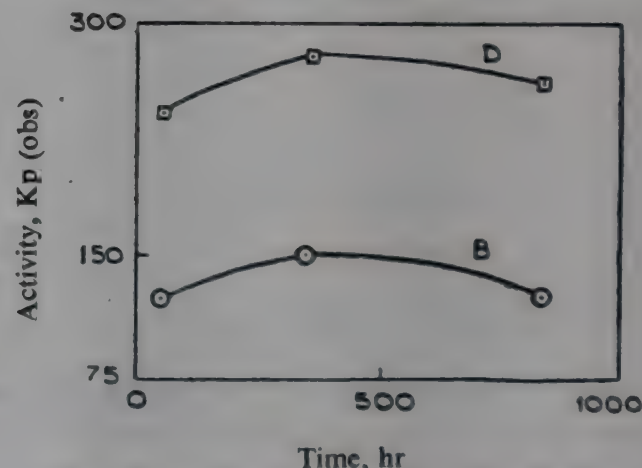


Fig. 4—Activity (K_p) as a Function of Time
[Plant/Pilot Plant Data]

TABLE 4—ACTIVITY—BENCH SCALE EXPERIMENT (EXIT GAS TEMPERATURE — 820°C)

Catalyst Type	System Pressure, kg./cm ² .	LHSV of Naphtha, g./g. cat.	H ₂ Naphtha vol./vol.	Steam/Carbon, mole/g.atom	Exit Gas Composition, %				Equilibrium Constant, $P_{CO} \times P_{H_2}^3 \times P^3$ $K_{p(obs)} = \frac{P_{CH_4} \times P_{H_2O}}{(\text{total moles})^3}$
					CO ₂	CO	H ₂	CH ₄	
A	10	0.35	0.25	5	11.8	14.4	67.2	6.8	9.82
B	10	0.70	0.25	4	10.0	6.2	66.8	7.2	14.04
				5	17.0	11.8	69.0	2.4	13.16
C	10	0.0	0.25	4	15.6	12.4	68.6	3.4	43.33
				5	17.2	10.8	69.8	1.8	47.75
D	10	0.70	0.25	5	15.4	12.6	69.0	3.0	52.48
				4	18.0	10.0	69.8	2.0	39.31
					15.6	15.8	66.6	2.2	69.16

TABLE 5—ACTIVITY—COMMERCIAL PLANT EXIT GAS TEMPERATURE, 820-850°C

Catalyst Type	Hours After Loading	System Pressure, kg./cm. ²	LHSV of Naphtha, kg./kg.cat.	Steam/Carbon mole/g.atm.	Temperature		Exit Gas Composition, % CH ₄ —CO—CO ₂ —H ₂	Equilibrium Constant $P_{CO} \times P_{H_2} \times P^2$ $\frac{P_{CH_4} \times P_{H_2}}{(total\ mol)^2}$
					Inlet	Outlet	$K_{p(oba)}$	
A	48	10	0.38	6.0	365	800-850	1.0-8.0-16.2-74.8	68.45
	360	10	0.38	6.5	380	-do-	1.6-8.2-15.8-74.4	34.85
	840	10	0.42	7.1	395	-do-	1.8-8.2-15.0-75.0	24.08
B	48	10	0.50	5.3	470	-do-	0.8-7.4-16.0-75.8	127.2
	360	10	0.58	3.5	460	-do-	2.0-8.4-15.0-74.6	152.4
	840	10	0.60	3.5	455	-do-	2.4-9.8-14.0-73.8	128.6
C	48	10	0.36	7.6	430	-do-	0.5-7.1-16.2-76.2	76.35
	360	10	0.42	7.4	420	-do-	0.46-7.8-15.6-76.1	96.23
	840	10	0.38	7.2	427	-do-	0.56-8.0-15.2-76.2	88.12
D	48	10	0.40	7.2	350	-do-	0.2-8.2-15.8-75.8	242.5
	360	10	0.42	4.2	340	-do-	0.17-8.1-16.0-75.7	279.1
	840	10	0.42	7.0	340	-do-	0.2-8.0-15.8-76.0	262.1

Plant Performance : Plant performance data collected at intervals during the life of the catalyst are presented in Table 3. The average plant conditions were as follows :

Pressure	10—12 kg./cm. ²
Inlet temperature	400—430°C.
Exit gas temperature	820—850°C.
Steam/Carbon	3.5 to 8.0.

Liquid space Velocity 0.36 to 0.60 kg./kg.cat./hr.

Hydrogen gas was introduced at the rate of 40 per cent by volume of naphtha.

DISCUSSION

From the chemical composition of the catalyst (Table 1), it is observed that the concentration of nickel oxide (NiO) of the different catalysts studied varies between 15.2 and 21.30 per cent. The results of the present investigation indicate that variation in nickel concentration within this range, which incidentally is the range of nickel in commercial catalysts, does not affect the activity. As such there is difficulty in considering nickel content as a parameter for selection of catalyst. In fact, the catalyst, having highest nickel content, showed the least conversion efficiency.

It is known that activity and stability of catalyst are not a function of active metal alone, nature of supporting materials,⁸⁻¹¹ which constitute the bulk of the catalyst plays a significant role. The carrier composition of the catalyst studied has wide variation. Alumina is the major constituent of all the samples and lime is present in different amounts in catalysts A, B and C. A contains TiO₂ as a major constituent while B has considerable amount of magnesia, silica and ferric oxide which are absent in other catalysts. Two catalysts, viz. B and C, containing minor amounts of alkali, show high loss on ignition at 900°C, whereas the corres-

ponding loss in weight in cases of A and D is very low. From the laboratory conversion data (Table 4) it can be seen that carrier composition cannot throw much light on their reformation efficiency. So far as conversion efficiency is concerned, it can be seen that all catalysts, except A, are more or less similar. The methane leakage is between 2.2 and 3.4 per cent at steam-to-carbon ratio 5. Thus, neither the nickel content nor the carrier composition can offer any guide for prediction of catalyst efficiency. Nevertheless, the chemical constituents may indicate their influence on stability of the catalyst. For example, the presence of alkali and alkaline-earth oxides may reduce the accumulation of carbon on the catalyst to account for better service period. On the other hand, upper limit of their concentration may be utilized as a guide-line for rejecting those showing fall in crushing strength, while in service due to higher degree of hydration.

Surface area of the catalysts studied ranges from 0.95 to 53.5 m²/g. It is expected that the conversion efficiency should have some relationship with surface area. From the data presented it can be seen that maximum conversion is associated with higher surface area. Observation is same in case of plant results with this catalyst. Lowest conversion is recorded for the catalyst having a minimum surface area. But the corresponding data for other catalysts does not show any linear relationship. Nevertheless, the data obtained is likely to tempt straight way acceptance of a catalyst with higher surface area. However, the fact that during use the surface area may undergo substantial change makes this point controversial.

Porosity of the catalyst (Table 2) appears to have some bearing on reforming activity. With the exception of catalyst A a higher pore volume is found to be associated with increased activity. Sample D, with pore volume 0.2653 cc./g., shows activity expressed

as equilibrium constant is of the order of 69.16, whereas B having minimum pore volume shows the corresponding figure of 43.33, which is minimum. Linearity of relationship between pore volume and conversion appears to hold when we consider B, C and D. That the above relationship does not hold good for catalyst A, suggests the necessity of examining the pore size distribution. On the basis of its average pore diameter 4365 Å and exceedingly small surface area, it may be stated that this catalyst mostly comprises macropores. It, therefore, appears that although pore volume can indicate potentiality of a reformer catalyst, it is necessary to examine the distribution of pores for getting a clear picture. Further, when only macropores account for the relatively high pore volume, the activity of the catalyst may not be as expected. Based on above discussion, it can be said that surface area, pore volume, average pore radius and pore size distribution data may be utilized for selection of industrially suitable catalyst.

For any reformer catalyst, mechanical strength is an important parameters and it may be affected by structural changes. It has been observed in earlier investigations that structural changes may be caused by heat and steam under reformer conditions⁷. It is desirable that the strength should not only be sufficient to withstand handling but also should have the capacity to stand dusting and crumbling which may be induced by the operating conditions. For the first part, strength of the fresh catalyst (Table 2) may provide adequate guidance. But most important property is the retention of strength in use and resistance to dusting. We know that dusting under reformer conditions leads to increase in pressure drop and cause appearance of hot tubes. It can be seen from Table 2 that mechanical strength of all the catalysts as such is quite high. The selection of catalyst with maximum mechanical strength however may not be always correct because the question of fall in strength while in service is there. Keeping in view the evidences regarding dependence of activity on surface area, and pore volume, let us see in the context of mechanical strength what is the prospect of catalyst D which has highest surface area, maximum pore volume and minimum pore diameter. This catalyst is having a crushing strength of 362 kg./cm.², which is quite high and acceptable for commercial use. The catalyst B, however, is having higher crushing strength of 452 kg./cm.² and its activity is also not very much different from that of D. It was, therefore, felt necessary from mechanical strength point of view to examine if their crushing

strength get changed under service conditions at different intervals of time. The results are shown in Fig. 2. It can be seen that crushing strength of D does not change either in steam or in reaction cycle whereas that of B sharply falls from 452 to 364, even in the environment of steam. This fall in crushing strength of B may be due to lime and magnesia which is present in the catalyst in appreciable quantity. It may be said that if the chemical analysis of a catalyst having high mechanical strength show appreciable concentration of alkali or alkaline-earth oxide, the possibility of hydration and consequent loss of mechanical strength under service conditions should be carefully examined.

Now on the basis of the above discussion, it may appear that all catalysts except A can be recommended for industrial use. Amongst these three catalysts, D and B were tested for change in activity for an extended period of 30 hours run. It can be seen from the data presented in Fig. 3, that there is practically no fall in conversion efficiency in both the cases. This provides additional support to the recommendations made.

To examine the validity of our evaluation all catalysts except B were put in commercial plant and the data obtained are presented in Table 5. The catalyst B was studied for efficiency in a pilot unit in same size (4" I D) tube for a period of 840 hours of continuous run. It can be seen (Table 5) that catalyst B was kept running at lower steam-to-carbon ratio.

This was done in consideration of alkali content of the catalyst. In plant operation however there was little scope of changing this steam/carbon ratio and it was much higher in accordance with the design of the particular plant. It can be seen from Table 5 that in reality all the three catalysts, viz. D, B and C, performed well in commercial/ pilot units. The change in concentration of methane at the exit after initial fall does not change to any great extent between 360 to 840 hours of run. The catalyst A in the plant also proved unsuitable.

Regarding the order of conversion efficiency we find that catalyst D is the best in laboratory as well as in plant. However, the relative position of B and D (in laboratory and plant) in order of conversion efficiency expressed as corresponding equilibrium constant are interchanged. But it can be seen from the gas analysis figures that the order of efficiency in terms of methane leakage for both the catalysts in laboratory and plant are same. Along with the above observation if we keep in mind the fall in crushing strength of

catalyst B with time (Fig. 2) we are left with catalysts, namely C and D, for choice. Again between C and D the physico-chemical parameters are in favour of D because its surface area and pore volume are much higher than that of C. In addition as discussed before its range of pore is in the finer region may be considered as an added advantage.

Now in consideration of the presence of alkali and alkaline-earth oxides in C and keeping in mind the observations of various authors¹² in support of the necessity of these components for preventing accumulation of carbon, we find it difficult to place catalyst C in a position lower than that of D straight way. It is true that plant data upto 840 hours should normally be accepted as a safe guideline. But a careful watch of reformer performance very often shows that even after running with sustained activity for 3-4 months the efficiency shows signs of decline. This may also be accompanied with increase in pressure drop, appearance of hot tubes and also sign of suspended particles in the condensate at the exit of the reformer. It has also been observed while analysing plant data that two different catalysts behaving in the same manner initially may show different change with progress of operation. Finally, it may so happen that one catalyst is taken out of service after a few months whereas the other showing trouble-free operation for one year or more. Such situations can only arise if the "Solid state", i.e. the catalyst itself, undergo change in different manner while in operation. It is quite likely that the active component nickel in service may undergo change in its crystal size. The rate of growth of nickel crystallite in its turn is likely to depend on the phase composition as well as on the chemical constituents. The growth in size of nickel will tend to reduce the overall efficiency of the catalyst. It is quite possible that such a change instead of affecting all the associated reactions identically may have certain selectivity.

It is true that the merit of the laboratory data discussed above in selection of proper catalyst does not

show any discrepancy upto 840 hours run in commercial units, but the question remains whether these can completely fulfil the industrial requirement or in other words whether such assessment can satisfy the consumers. In the light of the above discussions we are of the opinion that the rate of growth of nickel crystallite under reaction condition and possibility of appearance of new phase in the system must be taken into consideration for making a fool proof assessment of the stability. Knowledge of these two parameters alongwith those studies included in the present investigation can probably be very safely used for correct selection of catalyst for industrial operation. These obviously reduce the time and expenditure on trial and pilot experimentations. Work in this direction alongwith the problems associated with arresting the tendency of growth of nickel crystallites in reaction conditions are under study in authors' laboratory.

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The reduction kinetics of the finely dispersed nickel oxide supported on alpha alumina obeys the first order decomposition relationship of Coats and Redfern throughout the temperature range studied. In the cases of poorly dispersed catalysts, reduction mechanism is altered after 20 to 30 per cent of the material being reduced. Initially, reduction occurs from the interaction of gaseous molecular hydrogen which is then followed by the dissociatively adsorbed atomic hydrogen at the nickel-nickel oxide interface. In the latter case, the reduction mechanism becomes autocatalytic due to the catalysed action of the surface nickel atoms. This process covers the maximum fraction of the reduction. After 90 per cent of the material is reduced, it becomes a diffusion-controlled process and requires low activation energy.

The plots of threshold-reduction temperatures versus nickel oxide contents give an U-shaped curve. At low metal concentration, the threshold-reduction temperature is high due to a strong support-metal oxide interaction, whereas at high nickel concentration, nickel oxide hills appear to be formed exposing slant surfaces. These slant surfaces resemble (111) planes, which are stabler than the other two types of low index crystal planes, viz. (100) and (110) respectively. The exposure of the (111) planes seems to be responsible for the high threshold-reduction temperature for these samples.

Characterization of the Surface Heterogeneity of Supported Nickel Catalyst Using Temperature Programmed Reduction Technique

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Introduction

Supported metal catalysts undergo much slower reduction during the activation process as compared to the reduction of the corresponding bulk phase oxides. This difference in the behaviour of the supported catalysts is attributed to the fine dispersion of the oxide over the support and to the support-metal oxide interaction. Thus, while the reduction of the bulk nickel oxide is an autocatalytic process¹, the mechanism is not necessarily the same for the supported catalysts.

Studies on the reducibilities of supported catalysts have been used in the past as a means for detecting the support-metal oxide interactions². De Lange and Visser³ suggested the formation of a nickel hydrosilicate, from the observed difficulty in the reduction of silica-supported nickel oxide. Hill and Selwood³ indicated a valence induction effect between the support and the oxide on the basis of the reducibility studies made on a series of supported nickel oxide catalysts using various carriers. They proposed a tripositive

electronic configuration for nickel ion supported on γ -alumina. Reinen and Selwood⁴ found that the method of preparation of the catalyst greatly influences its reducibility. Thus, the reduction of nickel oxide coprecipitated with silica commences at 370°C, whereas nickel oxide impregnated on alumina has a threshold temperature of 450°C. They also observed that the reduction of a nickel-silica impregnate is easier as compared to that of a sintered nickel-alumina impregnate. Holm *et al*^{5,6} observed similar results and concluded that the reducibilities of the supported nickel oxides are governed, among other things, by the method of preparation, nature of the support, heat treatment temperature and promoter concentration. The impurity levels and dopants in the supported catalysts also influence the reducibilities to a great extent^{7,13}.

The isothermal technique, often used for studying the reducibilities, can be useful when comparing a number of solids; but it does not give a comprehensive picture of the surface topography in terms of the various

surface states within the solid itself. The present authors noticed that under temperature programmed reduction conditions, a number of breaks are observed in the Coats and Redfern¹⁴ type plots for the activation energy measurements. These plots have been analysed with a view to explore the possibility of using the breaks in elucidating the nature of surface heterogeneity. It has been shown that these plots together with the threshold temperature profiles can provide valuable information regarding the surface energy states of the supported catalysts.

Review of the Earlier Work

Although supported catalysts are difficult to reduce at a lower temperature¹⁶, higher activation temperatures are generally avoided in order to check the nucleation of reduced nickel particles, because large crystallites expose less metal surface giving rise to an inefficient catalyst unsuitable for 'demanding or structure sensitive' reactions¹⁶. Therefore, it has now become customary to incorporate trace amounts of metallic platinum, palladium, osmium, iridium, ruthenium or copper in the catalyst to enhance the reduction rates of the catalyst at a relatively lower temperature. Bergh¹⁷ established that molecular hydrogen is less reactive than the gaseous atomic hydrogen. Thus, incorporation of trace amounts of a third component enhances dissociative adsorption of hydrogen resulting in an increased rate of catalyst reduction. Delmon *et al*⁸⁻¹⁰ observed the same effect in the hydrogen reduction of unsupported nickel oxide containing traces of promoters. Charcosset *et al*¹³ ascribed this phenomenon to the formation of some disordered superficial areas on the nickel oxide particles.

Benton and Emmett¹ investigated the reduction kinetics of unpromoted massive nickel oxide using the experimental technique of Pease and Taylor¹⁸. They concluded from this study that the reaction between hydrogen and massive nickel oxide is autocatalytic in nature and the reduction is catalysed by the reduced nickel particles present at the nickel oxide nickel interface.

Later, Bandrowski *et al*¹⁹ made extensive kinetic investigation on the hydrogen reduction of nickel oxide. They proposed a rate equation on the basis of their experimental data. According to them, the overall reduction rate of nickel oxide is given by the sum of two rates. The first rate is due to the direct

reaction of nickel oxide with the molecular hydrogen, while the second rate arises from the nickel catalysed reduction of nickel oxide. Nickel is known to adsorb a large quantity of atomic hydrogen and therefore dissociative adsorption of hydrogen seems to govern the second kind of rate. Bandrowski *et al* proposed the following kinetic equation:

$$r = k_1 (1 - \alpha) \cdot p^{0.43} + k_2 (1 - \alpha) \cdot \alpha \cdot p^{0.05} \quad (1)$$

where r is the overall rate of reduction expressed in gram moles of water formed per minute per gram mole of nickel initially present, k_1 is the rate of direct reduction of nickel oxide and k_2 is the rate of nickel-catalysed reduction of nickel oxide. In the equation 1, α represents the fraction of initial nickel and p is the partial pressure of hydrogen. They found that nickel catalysed reduction (k_2) predominates over the direct reduction (k_1) and that the ratio of $k_2/k_1 \approx 5$ approximately. The low order of 0.05 for nickel catalysed reduction may be ascribed to the fact that nickel dissociatively adsorbs large amounts of hydrogen so that in this case nickel-nickel oxide interface becomes saturated with active hydrogen atoms. This gives rise to a very high reduction rate and explains the autocatalytic nature of the reduction of massive nickel oxide observed by Benton and Emmett¹. Hauffe and Rahmel²⁰ attributed the induction period observed during reduction, to the formation of metallic nuclei which ultimately catalyse the reaction and thus supported the views of Benton and Emmett¹. Parravano²¹ studied the reduction of unsupported nickel oxide and explained from the view points of semiconductivity, physical properties, electronic states and non-stoichiometry of the material. The effect of γ irradiation on the rate of reduction has also been studied²².

The above review of the earlier work indicates that reduction rates for finely dispersed supported nickel oxide will differ from that in a bulky deposit on a carrier and also in the form of unsupported massive oxide because of the differences in the electronic energy states and chemistry. Therefore, from theoretical considerations it may be envisaged that supported bulky deposit of nickel oxide on alumina will behave as a mechanical mixture of the two phases. Thus, it is likely that such samples will resemble the unsupported massive nickel oxide in their reduction kinetics favouring autocatalytic reduction mechanism, whereas in the finely dispersed state, individual nickel oxide particles are separated from each other by high energy barriers of the bare surface of the support. Hence,

in these catalysts in spite of the presence of reduced nickel particles in the neighbourhood and also dissociative adsorption of hydrogen on them, nickel catalysed reduction of nickel oxide should not be favoured. The present investigation offers a new approach to elucidate the above propositions on the basis of the experimental evidence, obtained from temperature programmed reduction data.

Experimental

1. *Preparation of Samples*: The catalysts studied were prepared by multiple impregnation of α -alumina rods, precalcined in their powdered form at 1300°C, in a 10 per cent (w/v) nickel nitrates solution. The impregnated rods were dried and then calcined at 450°C for 6 hours. The nickel oxide mass was prepared by decomposition of nickel nitrate (A. R. Grade) under the same conditions.

2. *Reductions*: A weighed amount of the dry sample was taken in a glass bucket hanging from a two-section helical quartz spring enclosed in an all-glass housing. The changes in weight during reduction were observed through a micrometer-microscope. The balance had a sensitivity of 0.0148 mg. The sample was heated by a heater wound non-inductively over the sample-jacket. The rate of temperature rise was maintained at 5°C/min. by a calibrated auto-transformer. Electrolytic hydrogen was purified by passing it through a 'Deoxo' tube. The purified hydrogen was fed to the sample-chamber through an inlet at the top of the bucket. The steam formed during the reaction was carried over by the exit gas through an outlet at the bottom of the sample chamber. At least three reduction runs were made for each sample and only the reproducible data were used for the analysis.

The samples selected here ranged from finely dispersed nickel oxide supported on alumina to a bulky deposit and an unsupported massive material. In the finely dispersed state one can expect greater possibility for the carrier interaction with the nickel oxide particles to the carrier surface. On the other hand, the samples containing a bulky deposit of nickel oxide can overcome the influence of the support except for those which are at the interface of the two distinct phases. In such a case, the sample can be expected to behave like a mechanical mixture of massive nickel oxide and alumina.

Discussion of the Results

Coats and Redfern¹⁴ investigated the solid state decomposition reaction kinetics and derived rate

equations for decomposition reactions from the following considerations:

The rate of decomposition of a solid can be expressed as

$$\frac{d\alpha}{dT} = k (1 - \alpha)^n \quad \dots (2),$$

where α is the fraction of the solid decomposed at time t and n is the order of the reaction.

The rate constant, k , can be represented by the Arrhenius equation, $k = A. e^{-E/RT}$ $\dots (3)$,

where A , E and R have usual significance.

Thirdly, the heating rate, a , in degree/min. can be expressed as

$$a = \frac{dT}{dt} \quad \dots (4),$$

By combining the equations 2, 3, and 4 simplifying, the following equation for a first order decomposition reaction is obtained

$$\text{Log}_{10} \left[\frac{2.303}{T^2} \text{Log}_{10} (1 - \alpha)^{-1} \right] = \text{Log}_{10} \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad \dots (5)$$

A plot of $\text{Log}_{10} \left[\frac{2.30}{T^2} \text{Log}_{10} (1 - \alpha)^{-1} \right]$ Vs $1/T$ gives a straight line, the slope of which is $-\frac{E}{2.303R}$

Assuming the reduction of nickel oxide by hydrogen to be a kind of decomposition in reducing atmosphere, the validity of equation 5 can be examined.

Fig. 1A shows three Arrhenius plots for the first three catalysts prepared by 1, 2 and 3 frequencies of impregnation respectively. It may be seen in Fig. 1A that two catalysts obey the first order decomposition rate equation 5 over the entire range of temperature scanned in the experiments. Moreover, the Arrhenius plots show the ranges of α values, which signify that both the catalysts behave uniformly throughout the process of reduction. The apparent energy of activation for the reaction of hydrogen with nickel oxide supported on α -alumina was found to be 27.7 K.cal/mole. Of course, the energy of activation will depend

on the support interaction as well as the chemistry of the dispersed phase. The third catalyst shows three activation stages in the Arrhenius plot. Initially, the reduction process was of the first order with an activation energy of 36.6 K.cal/mole upto an value of 0.2 only. An increase in the activation energy in this sample may be attributed to the crystal growth of nickel oxide. The Arrhenius plot shows that the reaction rate is suddenly accelerated requiring less activation energy, 19.6 K.cal/mole, upto an α value of 0.82. It may be suggested that at this stage the rate of reduction is governed by the catalytic effect of the reduced nickel particles, because reduced nickel particles dissociatively adsorb large quantities of active hydrogen giving rise to a highly reactive nickel-nickel oxide interface. In such a case, it might appear that nickel catalyses the reduction of the crystalline nickel oxide phase. This is followed by a third activation step corresponding to 10.1 K.cal/mole in the Arrhenius plot.

Such a low activation energy indicates the presence of low energy nickel oxide particles, which might appear by the rupture of the nickel oxide crystallites.

Fig. 1B shows three more Arrhenius plots for the reductions of two supported and one unsupported nickel oxide samples. The supported samples were obtained from 8 and 9 frequencies of impregnation of α -alumina carrier. It is evident in Fig. 1B that these samples show three distinct activation steps during reduction. The differences in the observed initial activation energies, which reflect the variation in the energy states may be assigned to the varying degree of crystal growth in the nickel oxide in these samples. Although the reduction of the samples obeys an overall first order rate equation, the presence of three activation steps definitely indicates three different courses of reaction mechanism. The kinetics of reduction of the massive nickel oxide initially shows an

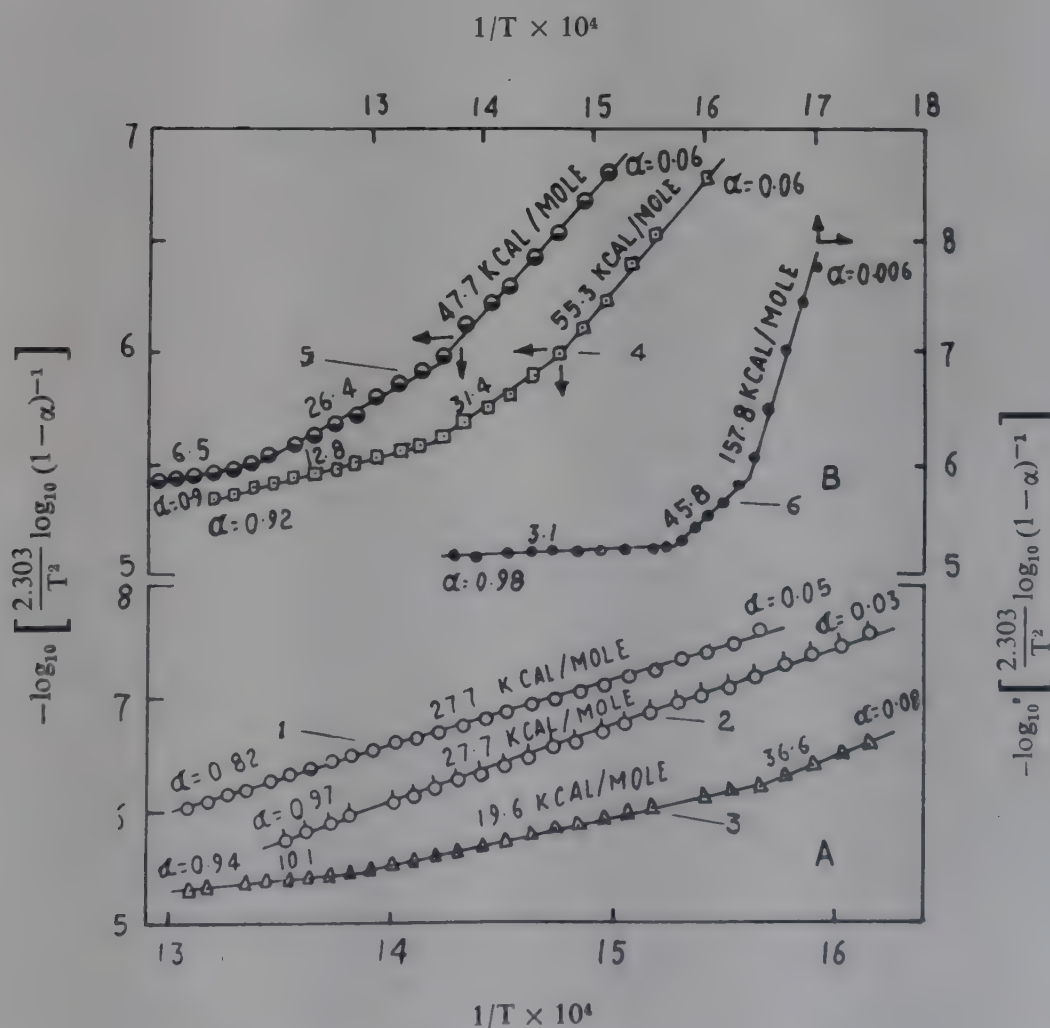


Fig. 1—Coats-Redfern Plots for Apparent Activation Energies

- | | |
|--------------|--------------------|
| 1. 1.4% NiO | 4. 17.08% NiO |
| 2. 2.15% NiO | 5. 18.90% NiO |
| 3. 4.27% NiO | 6. Unsupported NiO |

activation energy of 157.8 K.cal/mole only upto an α -value of 0.29. This activation energy accounts for the Ni-O bond as well as nickel oxide lattice energies. Moreover, in this case the process of reduction involves the interaction of gaseous molecular hydrogen with the weak sites in the nickel oxide lattice. This process is followed by nickel catalysed reduction of polycrystalline nickel oxide phase up to an α value of 0.92. It may be reckoned, therefore, that the nickel catalysed reduction of massive nickel oxide governs a major portion of reduction and the observed activation energy is 45.8 K.cal/mole found in this process. Towards the end of the reduction, the observed activation energy of only 3.1 K.cal/mole may accounted to be due to the reduction of molecular nickel oxide appearing after 90 per cent reduction of the material. The other two curves (Fig. 1B) also conform to similar analogies.

It can be summarized from the above consideration that finely dispersed nickel oxide (Fig. 1A) supported on α -alumina obeys the first order reduction kinetics with an activation energy of 27.7 K.cal/mole. As the crystalline character developed⁵ in the catalysts, three distinct activation stages become noticeable. These stages become more prominent with the progress of crystal growth (Fig. 1B) and the pattern of the plots approaches that of the massive nickel oxide. The Coats and Redfern¹⁴ relationship provides the verification of the order of the reaction. The data for each sample were, therefore, examined by substituting for $n = 0, 1/2$ and $2/3$ in the general equation and it was found that these multiple stages could not be reduced to a straight line. This shows that nickel oxide, whether supported or in the massive form, obeys first order reduction kinetics at least during the initial stage of the reaction. The variation in the nature of the plots from fine dispersion to massive form is evidently due to the nickel catalysed reduction of nickel oxide.

The small nickel oxide crystallites expose three types of low index crystal planes, viz. (100), (110) and (111). A calculation based on the lattice constant of nickel oxide to be 4.165 Å shows that the nickel densities in the planes (100), (110) and (111) are 2.88×10^{19} , 2.45×10^{19} and 4.01×10^{19} sites/m² respectively. Since the densest packing implies highest stability of the plane²³, nickel ions in the plane (110) will be the least stable. Thus, in the crystalline nickel oxide, the nickel ions in the (110) plane will be readily attacked by hydrogen and be reduced first.

Fig. 2 shows the observed temperatures during TGA runs at which reduction commenced for the various

samples. It is seen in the U-shaped curve that with the increasing frequency of the impregnation, there is a sharp change in the threshold reduction temperature for most of the samples. At low nickel concentrations, the observed high reduction temperatures may be attributed to the metal-support interaction. With the increasing nickel concentration the reduction temperature approaches that of the unsupported nickel oxide till there is a further sharp increase. From earlier investigations¹⁵, it is known that at higher metal concentrations nickel oxide hills are formed on the carrier. A slight increase in the BET surface areas was found in these samples. If nickel oxide forms such spikes, it exposes slant surfaces resembling (111) planes of a face centered cubic lattice²⁴. These (111) planes are more stable than the other two types of low index crystal planes. Thus, at low metal concentrations, owing to a flat type distribution of nickel oxide molecules, the exposed crystal surface contains 1:1 ratio of (110) and (110) planes, which are less stable than the (111) planes. However, higher threshold temperatures observed for the catalysts having low metal concentrations are obviously due to the predominating metal-support interactions. At higher metal concentrations, although the nickel oxide molecules, away from the support surface, overcome the influence of the support and are in the massive form yet these are also difficult to reduce because of the exposure of the stable (111) planes.

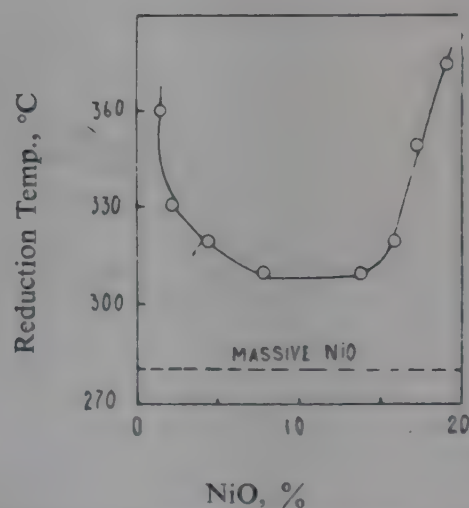


Fig. 2—A Plot of Threshold Temperature vs. Nickel Oxide Concentration

[The broken line is for the unsupported nickel oxide]

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A commercial catalyst must have a good mechanical strength to withstand abrasion and shock during handling and use. Tableting by compression of solid granules is a widely adopted technique for giving shape and strength to many commercial catalysts. An attempt has been made here to study the factors influencing the mechanical strength of alumina pellets prepared by compression of solid granules. The effect of moisture content, grain size, compression load and nickel nitrate concentration in binding liquid on the compressive strength as well as other physical properties, like, surface area and pore size distribution, have been studied. The following observations have been made: (1) for any grain size there is an optimum moisture requirement for maximum strength of alumina pellets. While the maximum strength of a pellet under a fixed compression load is almost independent of grain size within the range studied the optimum moisture increases with increase in grain size; (2) progressive drying of pellets containing higher moisture results in gradual increase in strength until a constant maximum is reached; (3) increase in compression load results in a higher strength of pellets until a limiting value is reached, the effect being more prominent with bigger granules; (4) incorporation of nickel nitrate solution in place of water as a binding liquid gives better strength to the pellets; the strength increases with increase in concentration of nickel nitrate in the binding solution; and (5) surface area and pore size distribution of the dried pellets remain almost unchanged with the variation of grain size and compression load. However, both the parameters decrease with increase in concentration of nickel nitrate in the binding solution.

A Study on the Mechanical Strength of Alumina Pellets

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Introduction

One of the prerequisites for an industrial catalyst is a good mechanical strength of the pellets. In spite of better activity and selectivity a catalyst may not find application in industrial reactors if it does not possess the required strength. Hence, studies on the processes involved in giving shape and strength to catalyst pellets are of vital importance. The mechanical strength can be imparted to a solid by a number of methods, like (i) granulation of fine powder in presence of a liquid, (ii) kneading fine powder into a paste with a liquid and extruding the paste through a die head, (iii) compression of small granules into tablets, etc. The ultimate aim of any process is to create a better force of attraction amongst the solid particles. The third method mentioned above is the most widely adopted one in the commercial manufacture of catalyst pellets.

The aim of the present investigation is to study the factors involved in influencing the mechanical strength of solid pellets prepared by compression of small granules. This investigation includes studies on the effects of grain size, compression load, amount

of binding liquid and concentration of nickel nitrate in the binding liquid on the strength of alumina tablets. In addition, physical parameters like intergranular void space, surface area, pore volume and pore size distribution of the tablets have also been studied.

Experimental

Commercially available calcined alumina, containing more than 98 per cent α -alumina, was used in the present investigation. The coarse alumina was ground to a fine powder. Nickel nitrate used for impregnation was of 99.9 per cent purity and was prepared by dissolving pure metallic nickel in pure nitric acid followed by fractional crystallization.

Preparation of Tablets: Finely powdered alumina was made into a uniform paste with distilled water, subjected to atmospheric drying for 24 hours and then fed to a granulating machine. The granules were separated into the following four sizes (BS. sieves) for the investigation; —12+16, —25+30, —30+60 and —60+100 mesh, and designated as A, B, C and D respectively. The initial moisture content of the granules was maintained around 16 per cent and then

varied downward by slow drying at 80° C. The wet granules with different moisture content were compressed to tablet in a tableting machine* having devices for precise adjustment of depth of fill and compacting load. The depth of fill was kept fixed at 16 mm. and tablets were made into solid cylindrical shape having 10 mm. diam. and 10 mm. height. The compacting pressure was varied between 1000 and 6000 kg./cm².

In order to see the effect of nickel nitrate solution as binding liquid in place of pure water, two samples (AN1 and AN2) of granules of -12+16 mesh size were prepared using nickel nitrate solutions with 5 and 10 per cent nickel content during pasting. They were partially dried to maintain 10 per cent moisture content and then tabletted under different compacting pressure.

Crushing Strength: The crushing strength of the tablets were determined immediately after tableting and also after drying at 120°C for 15 hours. The moisture content of the tablets could be calculated from the loss in weight of the tablets after drying. A Hounsfield tensometer was used for the determination of strength of tablets. A tablet was placed between the anvils and the load was applied as uniformly as possible until the breaking load was indicated. For each sample, the strength of at least 10 tablets was determined and the maximum variation observed was within ± 2 per cent.

Physical Parameters: To study the influence of grain size and nickel concentration in the binding liquid on the physical structure of alumina pellets, physical parameters, like intergranular void fraction, specific surface area, percentage pore volume and pore size distribution of some of the samples of dried tablets, were determined by the standard laboratory techniques.

The intergranular void fraction, is given by the relationship, $\epsilon = V_G - V_H$, where V_G represents geometric volume of a tablet per unit gram and V_H represents mercury displacement volume per unit gram. The dimensions of a tablet were measured by a traveling microscope. The total volume of a tablet, calculated from these dimensions, was divided by weight of the tablet to obtain the value of V_G . The original granules corresponding to different tablet samples have been used after complete drying for determination of mercury displacement volume.

Specific surface area was determined by the conventional BET method by the adsorption of nitrogen at -196°C.

The pore volume was determined by the difference of mercury and helium displacement values. For the pore size distribution a mercury porosimeter (Aminco model), having a pressure range upto 5,000 lb/sq. inch was used.

Results and Discussion

In the present investigation the granules have been assumed to be spherical and the average size for any sample of granules has been assumed to be the diameter corresponding to the mean of the openings of standard meshes used for grading of size.

Effect of Initial Moisture: Fig. 1 illustrates the effect of variation of moisture content on the crushing strength of alumina tablets made by compression of different sizes of granules. In making these tablets compression load was maintained constant at 4000 kg./cm². It is interesting to note that for all grain sizes, with increase in moisture content the strength gradually increases, reaching a maximum value and then starts falling. Also, it can be seen that there is no appreciable difference in the maximum strength of tablets attainable with different particle sizes at a constant compression load. However, there is a shift in the maximum of the curve towards right (Fig. 1) as the average particle diameter increases. In other words, bigger grains need more moisture to attain the maximum tablet strength. Thus, for the grains in the range -12+16 mesh, the optimum moisture content is found to be about 10.8 per cent, whereas for the particles in the range -60+100 mesh the same is observed to be as low as 4.2 per cent. Yamadaya *et al*¹ reported an optimum moisture content of 10 per cent on alumina for the maximum strength. But he has not mentioned about the particle size of the alumina.

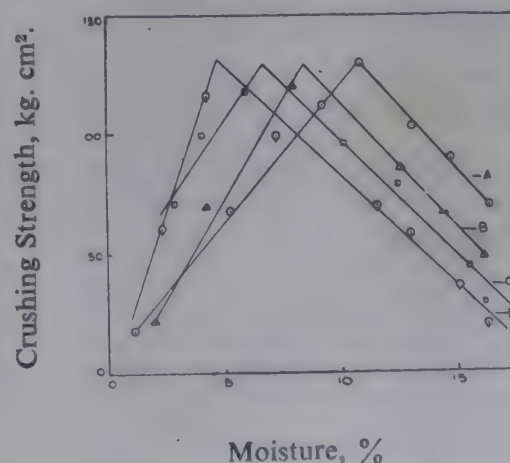


Fig. 1—Variation of Crushing Strength with Moisture Content

*Kililan's DPID model

The above observations can be explained on the basis of the models suggested by Newitt and Conway-Jones². According to these models, the interparticular bonding force, on which depends the tensile strength of the aggregate, varies with the moisture content and attains a maximum at an optimum moisture content, the value of which depends on the intergranular void volume. Since in an aggregate of bigger grains the intergranular void volume is more which is evident from the results (Table 1), it is quite natural that to attain a state corresponding to the maximum bonding strength the bigger grains will require more moisture.

In order to examine the effect of gradual removal of moisture from the wet tablets on their crushing strength, a sample of alumina tablets prepared from -60+100 mesh grain size with a moisture content of 16 per cent was subjected to slow drying at 80°C and the moisture content and crushing strength of the tablet at certain intervals was determined. The crushing strength of the tablets at different stages of drying was plotted against the corresponding moisture content of the tablets (Fig. 2). The nature of the curve indicates that there is a progressive increase in strength as the moisture content decreases. From the slopes of curve at various points, it is also observed that the rate of increase in strength is more in the region of high moisture content and is negligible at very low moisture content. This can be explained on the basis of the pendular bridge model, suggested by Newitt and Conway Jones² (Fig. 3). According to these authors², the strength of a single pendular bridge is given by, $S_T = \pi bT(3 + b/c)$, where T is the surface tension of the liquid and 'b' and 'c' are defined in Fig. 3. As moisture is gradually removed by drying, the grains are drawn closer due to surface tension and consequently the radius of curvature 'c' and the value of 'b' in Fig. 3 decrease, but the former decreases more rapidly than the latter. This causes increase in intergranular bonding force thereby increasing the strength of the tablet.

Effect of Tableting Load: Fig. 4 shows the effect of tableting load on the crushing strength of alumina tablets starting from different grain size with a con-

stant moisture content of 16 per cent. For this purpose the tableting pressure was varied from 1000 to 6000 kg./cm². It is observed from the curves that for all grain sizes the strength increases with increase of compacting pressure until it reaches a limiting value. Application of pressure brings the grains closer together resulting in higher intergranular bonding force. Ultimately, a situation arises when the maximum possible compactness of the grains is achieved and further increase of pressure will have no effect. This was also observed by Yamadaya *et al*¹, who made similar studies on alumina pellets. Various other authors³⁻⁹ have also reported the influence of compacting pressure on different heterogeneous catalysts.

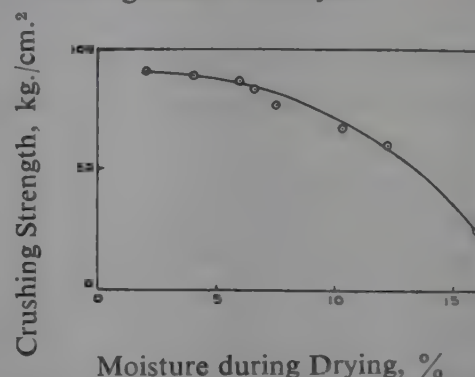


Fig. 2—Variation of Strength During Progressive Drying

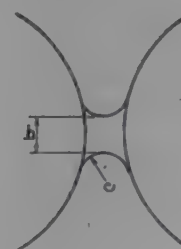


Fig. 3—Pendular Bridge Model

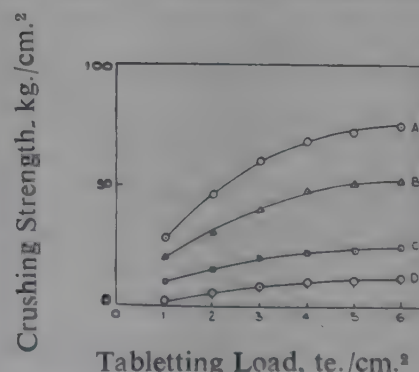


Fig. 4—Variation of Strength with Tableting Load

TABLE 1—SURFACE AREA, VOID VOLUME, PORE VOLUME AND PORE SIZE DISTRIBUTION OF DIFFERENT GRAIN SIZE TABLETS

Sample	Geometric Volume, cc./g. V_G	Mercury Displacement Vol., cc./g. V_H	Void Fraction, cc./g.	Pore Volume, cc./g.	Pore Size Distribution, vol% ($\text{\AA}$)					Surface Area, m ² /g.
					4-175	175-300	300-400	400-500	500-75000	
A	0.6868	0.5716	0.1152	0.2956	48.5	11.1	8.9	6.7	24.8	71.1
B	0.6462	0.5692	0.0770	0.2927	52.8	11.3	7.4	4.9	23.6	69.6
C	0.6140	0.5687	0.0453	0.2920	63.3	11.5	2.7	1.1	21.4	66.1
D	0.5824	0.5688	0.0136	0.2880	55.8	12.2	6.2	3.8	22.0	68.0

It is also observed from Fig. 4 that the effect of pressure is more in case of bigger grain sizes, which appears to be due to the fact that the assembly of bigger grains possesses more intergranular void space (Table 1), thus rendering the influence of compacting pressure more effective.

Effect of Nickel Concentration in the Binding Liquid: Instead of using pure water as the binding liquid, sometimes a salt solution is used for that purpose, specially when a particular salt has to be impregnated to a carrier material. Considering wide range of application of alumina-nickel oxide system as industrial catalysts, nickel nitrate solutions were also used in place of water as the binding liquid. The effect of concentration of nickel in the binding solution used for tableting alumina grains ($-12 + 16$ mesh) on the tablet strength is illustrated in Fig. 5. It is evident from the curves that increasing concentration of nickel in the binding liquid increases the strength of the tablets. The increase in strength of alumina pellets due to incorporation of nickel nitrate in the binding liquid appears to be due to the fact that surface tension of nickel nitrate solution is higher than that of pure water which results in higher intergranular bonding force as per the mechanism suggested by Newitt and Conway Jones². Yamadaya *et al*¹ also indicated that the mechanical strength of

pellets prepared from some impregnated alumina is higher than that of pure alumina pellets.

It is also observed from the curves (Fig. 5) that on drying, the tablets with higher nickel concentration in the binding solution gain more strength. This appears to be due to the fact that with higher initial concentration of nickel, the rate of increase in nickel concentration on drying will be more resulting in a higher rate of increase in surface tension of the binding medium.

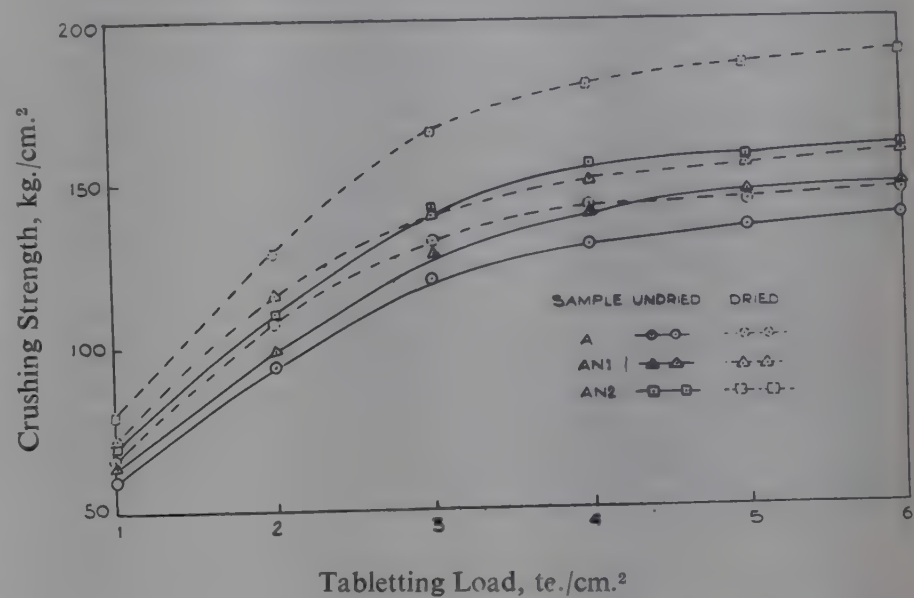


Fig. 5—Effect of Nickel Concentration and Tableting Load on Strength of Undried & Dried Tablets

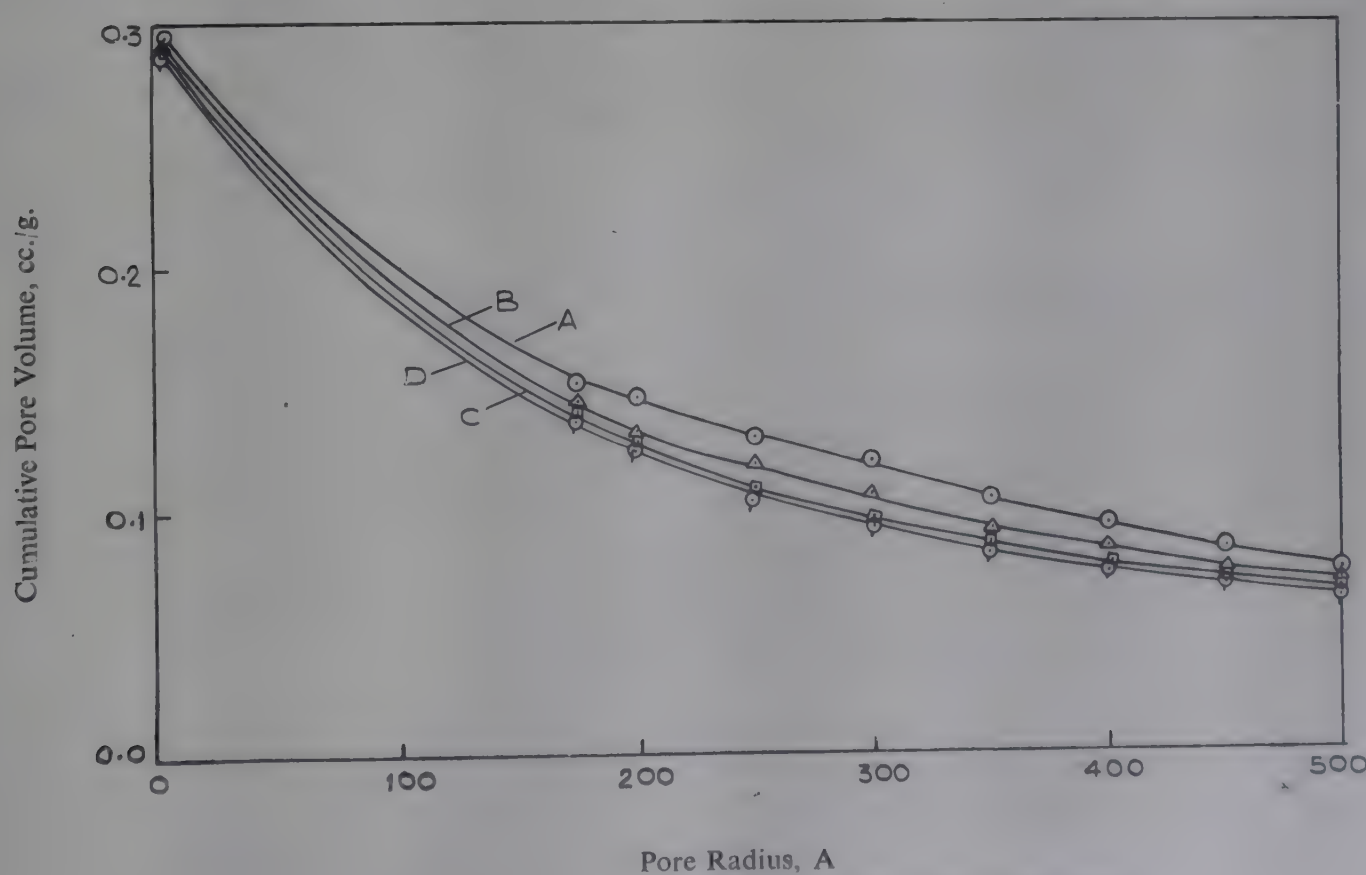


Fig. 6—Cumulative Pore Volume of Different Size Granules

TABLE 2—SURFACE AREA, PORE VOLUME AND PORE SIZE DISTRIBUTION OF SOAKED TABLETS

Sample	Pore Volume, cc./g.	Pore Size Distribution, vol % (Å)					Surface Area, m ² /g.
		4-175	175-300	300-400	400-500	500-75000	
A	0.2956	48.5	11.1	8.9	6.7	24.8	71.1
AN-1	0.2360	38.1	18.2	10.6	7.6	25.5	57.9
AN-2	0.1859	43.1	16.8	11.6	10.3	18.2	48.8

Effect on Physical Parameters: The results of experiments on various physical parameters, like intergranular void fraction, specific surface area, pore volume and pore size distribution, of some of the dried tablet samples are given in Tables 1 and 2, and also in Figs. 6 and 7. The intergranular void fraction in a pellet increases with increase in grain size. Surface area, pore volume and pore size distribution (Fig. 6) of the alumina pellets appear to have marginal dependance on grain size when water is used as binding liquid. This is quite expected because the individual grain structure on which depend the surface area, volume of finer pores and pore size distribution, is same due to the fact that the starting material and history of preparation of the granules of different sizes are same.

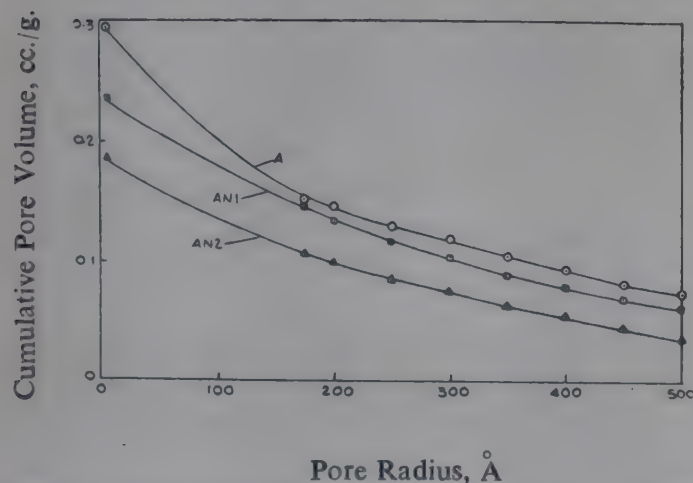


Fig. 7—Cumulative Pore Volume for Granules with Different Binding Liquid

With increase in nickel concentration in the binding liquid, there is a definite fall in both surface area and pore volume. It can be seen from Table 2 and Fig. 7 that there is considerable change in pore size distribution on incorporation of nickel nitrate in the binding liquid. All these changes in the physical parameters due to incorporation of nickel nitrate appears to be due to the fact that nickel nitrate will be deposited on the pore wall on drying and will cause change in the pore structure and surface area.

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In this investigation, the effect of heat treatment on physical and structural characteristics of copper-kieselguhr catalyst and their influence on dehydrogenation activity have been studied. The structural properties of the catalyst changed sharply at 600°C. The surface area and pore volume of the catalyst dropped from 79.6 to 3.3 m²/g. and 0.898 to 0.548 cc/g. respectively as the curing temperature was increased from 600 to 800°C. In the same temperature range, bulk density increased from 0.6 to 0.8 g./cc. and particle size from 500 to 800 Å. The mechanical strength also increased from 80 to 180 kg./cm². The catalyst cured at 200-300°C showed maximum activity but upto 600°C it gave a fairly good conversion.

Effect of Calcination on Physico-Chemical Parameters and Activity of Copper-Silica Type Dehydrogenation Catalyst

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Introduction

It is known that structural and textural properties have a definite role in determining specific activity and selectivity of a catalyst. Specific surface, pore volume, particle size and pore size distribution are dependent on the methods of preparation as well as chemical composition. The desired structural characteristics can be attributed to a catalyst by adopting a suitable preparative technique.

The incorporation of active ingredients on a suitable carrier and sintering have been used as an effective method in catalyst preparation¹⁻³. The supports increased thermostability of a catalyst and arrest crystal growth⁴. The effect of support and the nature of active ingredients on activity for dehydrogenation of alcohol to acetaldehyde have been reported in literature⁵⁻⁷. But a systematic study on the effect of sintering on structural properties of supported copper catalyst has not been reported so far.

In the present investigation, a catalyst has been prepared by the deposition of copper on kieselguhr and heat-treatment at different temperatures. The changes in the physical and structural properties caused by such a treatment have been evaluated and discussed.

Experimental

The catalyst was prepared by the precipitation of a copper compound on a kieselguhr support. Powdered kieselguhr was suspended in caustic soda solution heated to 60-70°C. The suspension was vigorously stirred and to this the requisite quantity of copper nitrate solution was added. pH of the media was finally adjusted to 7 (± 0.5). The slurry was filtered and washed with distilled water till free of nitrate and then dried at 120°C for 11-12 hours. The dry cake was granulated and then tabletted to 10×6 mm. size. The tablets were heated to 100, 200, 300, 400, 600 and 800°C respectively for a duration of 4 hours. The finished catalysts were marked serially as I, II, III, IV, V and VI in the increasing order of heat treatment temperature.

For characterization, the samples were examined for phase composition, mechanical strength, surface area and pore size distribution. Their phase composition was examined by DTA and TGA and mechanical strength was determined by a Hounsfield tensometer. An average of 10 tablets were taken as the representative mechanical strength of the sample. The volume of the tablets was measured by water displacement, surface area by BET method and pore size distribution by Aminco Winslow porosimeter with a range of 0-15000

psi. The pore radii were calculated from the equation $2r = \frac{175}{P}$, where r is the radius in microns and P is the pressure in psi.

DTA thermogram were taken at a heating rate of $10^\circ\text{C}/\text{min}$. using ignited alumina as the reference material in an assembled DTA unit consisting of a Gallenkamp furnace, a Bousch and Lomb recorder and Ether tranistoral programmer.

For TGA study about 160 mg. of sample was non-isothermally heated at a rate $6.5^\circ\text{C}/\text{min}$. in a Stanton mass flow thermo-balance with a sensitivity of 0.2 mg./division. DTA and TGA studies were carried out under atmospheric conditions and in a temperature range $100\text{--}800^\circ\text{C}$.

The activity of the samples were determined in an apparatus similar to one used in earlier investigation⁵. Conversion of alcohol to aldehyde was determined in the temperature range of $270^\circ \pm 5^\circ\text{C}$, atmospheric pressure and flow rate 4.5 ml. of alcohol/ml. of cat./hr. For complete condensation of acetaldehyde chilled water at $3\text{--}5^\circ\text{C}$ was passed through the double-walled condenser.

The analysis of the product was done by using hydroxylamine hydrochloride which reacts quantitatively with acetaldehyde according to the following reaction.



The acid liberated is titrated against standard sodium hydroxide (N).

Discussion

Supported copper catalyst is used for dehydrogenation of ethyl alcohol to acetaldehyde in the temperature range $250\text{--}310^\circ\text{C}$, atmospheric pressure and a flow rate of 4-5 ml. alcohol/ml cat. /hr. The total active life of the catalyst is realized in $3/4$ cycles. At the end of each cycle, the catalyst is regenerated by oxidation followed by reduction. The oxidation of the catalyst by air is highly exothermic and unless carefully controlled there are chances of temperature runaway which may result into deactivation. The objective of the present investigation is to determine the changes that occur in the structural properties of catalyst on heat treatment.

Porosity and Pore Size Distribution: The porosity and psd data are presented in Table 1 and Fig. 1 respectively. Porosity increases continuously reaching a maximum at 600°C , but drop substantially at 800°C . At 600°C where porosity attains a maximum, it is presumed that release of structural water and decomposition of

salts are complete. DTA and DTGA results confirm this observation. It can be seen that porosity of the catalyst cured at 800°C dropped by about 30 per cent when compared with the catalyst cured at 100°C .

The pore size distribution has been presented as $\frac{dv}{dr}$ vs $\bar{r}$ in Fig. 1. In all the samples there is a regularity in distribution pattern of the curve as the curing temperature is increased from 100 to 800°C . But the area of the peaks diminishes as the temperature of curing rises. At the lowest temperature of curing, the curve has a single sharp peak at $32 \text{ \AA}$ and beyond this point the pore volume is covered by pores having wider size. As the temperature of curing is raised the curves are flattened and at the same time new peaks appear on the right hand side. In case of samples cured at 200, 300 and 400°C , two sharp peaks appear at $(32 \text{ \AA}, 86 \text{ \AA})$, $(32 \text{ \AA}, 86 \text{ \AA})$ and $(60 \text{ \AA}, 80 \text{ \AA})$ respectively. But with samples cured at 600°C there are three peaks at 60, 86 and $210 \text{ \AA}$. Sharp contrast is observed in case of sample cured at 800°C . There are two small peaks at $70 \text{ \AA}$, but the areas under the peaks are very small. Sharp distribution and aggregation of pores in specific region as observed in case of sample cured at lower temperatures are missing when the catalyst is heat treated at 800°C and $\frac{dv}{dr}$ remain almost unchanged with increasing $\bar{r}$.

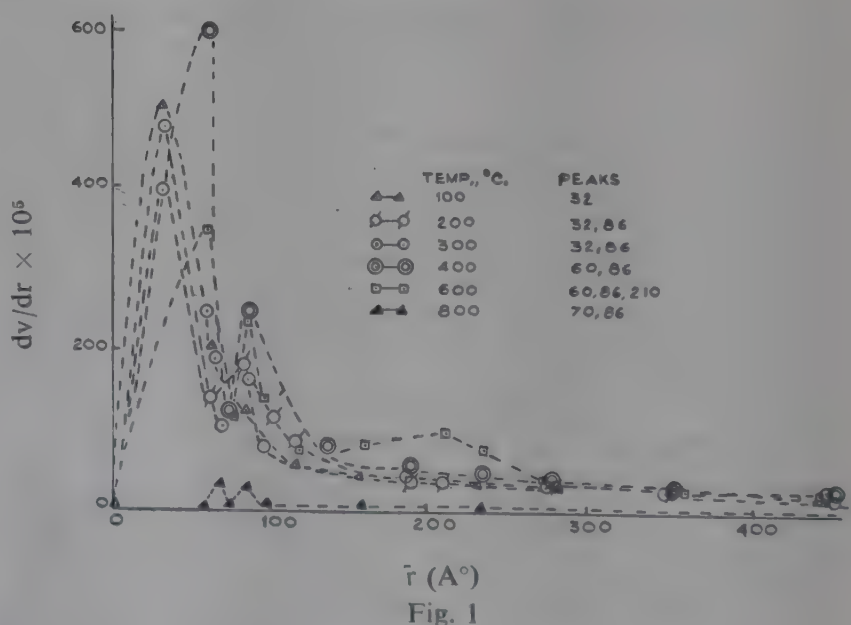


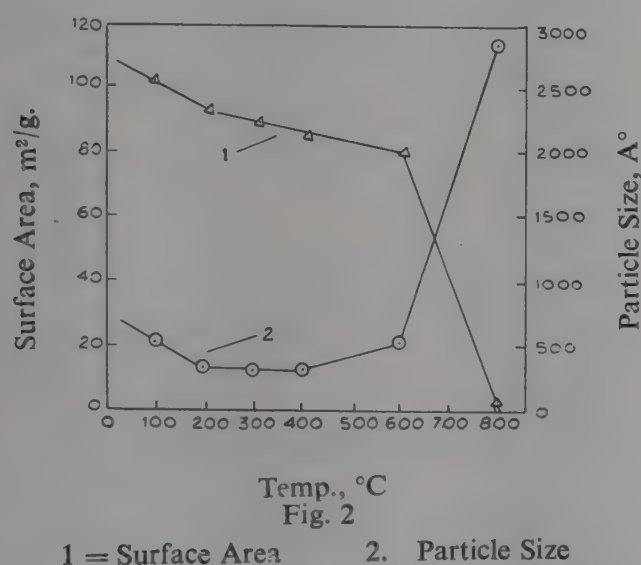
Fig. 1

Surface Area and Particle Size: The results of surface area and particle size are presented in Fig. 2. It may be observed that the specific surface area decreases continuously with increasing temperature with a sharp break at 600°C . In contrast particle size remains practically unchanged below 400°C . But at 400°C increase in particle size is about 80 per cent and it is

TABLE 1

Sample No.	He. Displacement, cc./g.	Hg. Displacement, cc./g.	T. P. V. cc./g.	Porosity, cc./100 cc.	Pore Size Distribution, % by volume						
					4-60, Å	60-100, Å	100-200, Å	200-300, Å	300-400, Å	400-500, Å	500-75000, Å
I.	1.0110	0.2936	0.7174	71.0	33.4	7.7	7.3	4.8	3.2	3.0	40.6
II.	1.109	0.2606	0.8403	76.5	30.1	7.3	8.6	5.5	3.5	4.0	41.0
III.	1.0926	0.2264	0.8262	75.6	26.8	7.4	8.2	5.1	3.7	3.3	45.5
IV.	1.117	0.2405	0.8787	78.8	22.0	8.3	7.7	5.7	3.5	2.7	50.1
V.	1.1267	0.2389	0.8878	78.8	21.4	6.4	7.1	4.7	3.2	2.6	54.6
VI.	0.7943	0.2466	0.5477	68.9	17.3	0.4	1.2	0.5	0.9	0.4	78.9

ninefold at 800°C. There is a sharp drop in surface area from 70.6 to 3.3 m²/g. as the temperature of curing is raised from 600 to 800°C.



It was expected that the surface area will increase with the expulsion of volatile matter from the catalyst as the temperature was raised followed by decrease due to sintering at higher range of temperature. But contrary to expectation there was drop in specific surface area even with release of the moisture and decomposable products from the catalyst as the curing temperature was increased. This might occur if with the expulsion of moisture and gaseous products, the walls of the pores collapse and finer pores are replaced by wider ones. In such a case the expected rise in surface area might not occur. Reduction of surface area above 600°C must have occurred due to sintering of the mass. This was supported by the corresponding increase in particle size, drop in pore volume and disappearance of finer pores from the catalyst.

Differential Thermal and Differential Thermogravimetric Data : DTA and DTGA data are presented in Figs. 3 (A & B), 4(A & B) and 5.

Purified kieselguhr dried at 100-120°C exhibited a low temperature endothermic peak at 140-150°C due to

release of strongly bound water from the mass (Fig. 4A). Above this temperature the thermogram did not return to zero line but ran with a downward slope up to 900°C. The slow gradient indicated that expulsion of water takes place in a wide temperature range. This observation was supported by the TGA (Fig. 5) data on kieselguhr. It was found that about 3.75 per cent of water is released at 140-150°C. But as the mass was heated further, it lost its weight slowly and the process continued up to 900°C. The total loss of weight was 6.6 per cent in the range 150-900°C.

The air-dried copper hydroxide showed endothermic peak at 100°C because of decomposition of the hydroxide (Fig. 4B). Above this temperature the thermogram ran parallel to the temperature axis showing that up to 900°C there is no further constitutional change in the oxide (Fig. 4B) involving change in weight.

The study of the thermogram of the catalyst (Fig. 3A) showed that low temperature endothermic peaks of copper hydroxide and kieselguhr observed at 100° and 140-150°C respectively are missing in the thermogram of the catalyst. There were two distinct peaks in the range of 180-200°C and 250-320°C. The endothermic peaks at higher temperature were indicative that due to structural change release of water at low temperature was restricted in the catalyst. Above 320°C there are two exothermic peaks; one at 490-520°C was rather flat and the other between 710 and 740°C was quite distinct. DTGA curve (Fig. 3B) of the catalyst showed about 5, 10 and 8 per cent loss in weight at the temperatures 90-110, 200-300 and 400-500°C respectively. It was expected that corresponding to 8 per cent loss in weight there should have been an endothermic peak in the thermogram in the temperature range 400-500°C but this peak was absent. It may be that intensity of exothermicity for the process of crystallization and sintering had masked the endothermic behaviour for the expulsion of constitutional water. The DTA curve

showed that there is a distinct constitutional change between 710 and 750°C. Drastic reduction in surface area and pore volume showed that the change above 700°C must have been caused due to sintering of the catalyst. It was found that the catalyst prepared by curing between 200 and 300°C had the highest conversion efficiency. It appeared that the activity of the catalyst was fully developed after the expulsion of the constitutional water. Heat treatment above 300°C slowly eliminated the active sites probably due to particle growth. Industrial experience also confirmed that a copper catalyst showed the best performance in the temperature range 250 to 300°C.

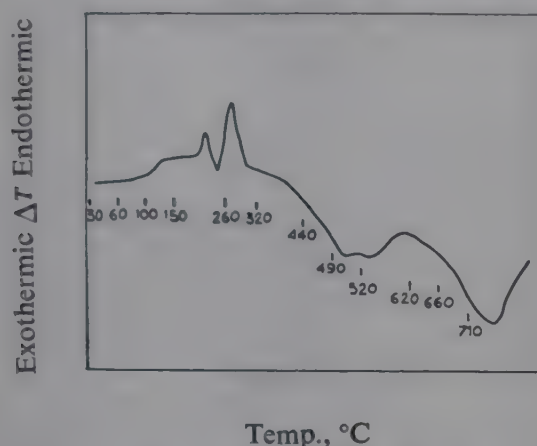


Fig. 3A—DTA Thermograms of Catalyst

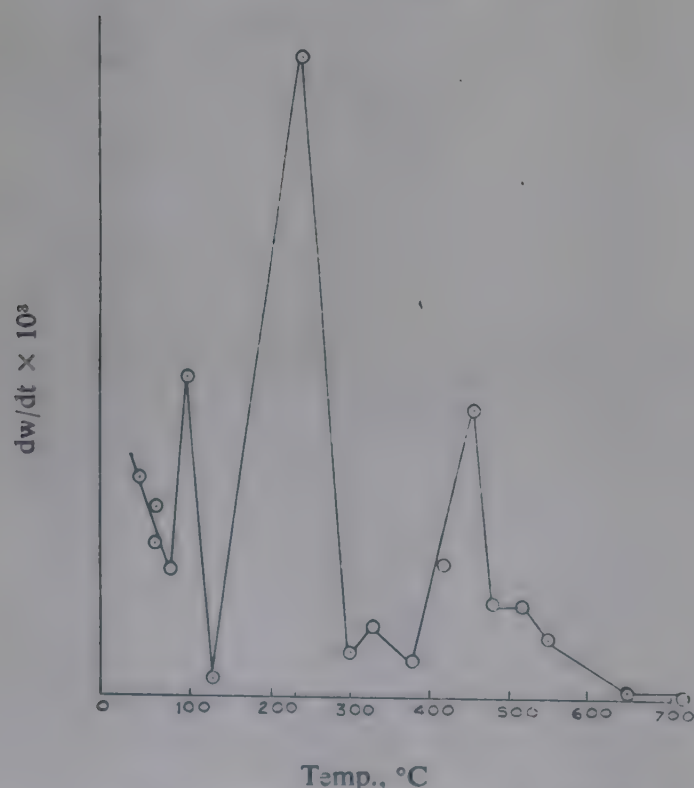


Fig. 3B—DTGA Thermogram of Catalyst

TGA thermograms of copper hydroxide, kieselguhr and the catalyst are presented in Fig. 5. It showed that the copper compound precipitated as above was not a pure copper hydroxide. The total loss in weight was only about 7-9 per cent which corresponds to 35-40

per cent copper present as hydroxide. The remaining portion of the copper was likely to be present as oxide. Kieselguhr lost about 10 per cent of its weight at 900°C. But the TGA curve of the catalyst where copper hydroxide precipitated on kieselguhr was quite different from what might be expected from their mechanical mixture which implies that either there has been interaction between support and copper compound or the copper is precipitated as hydroxide only. If it was assumed that the loss from kieselguhr which constituted 50 per cent of the catalyst the mass remains constant around 10 per cent then the loss from copper compound is much above 18 per cent which theoretically corresponds to 100 per cent hydroxide. A higher percentage of volatiles released from the catalyst indicated that the particles got hydrated during the process of precipitation.

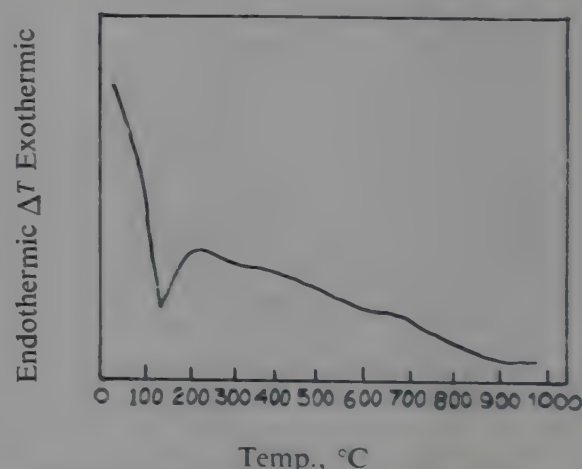


Fig. 4A—DTA Thermogram of Kieselguhr

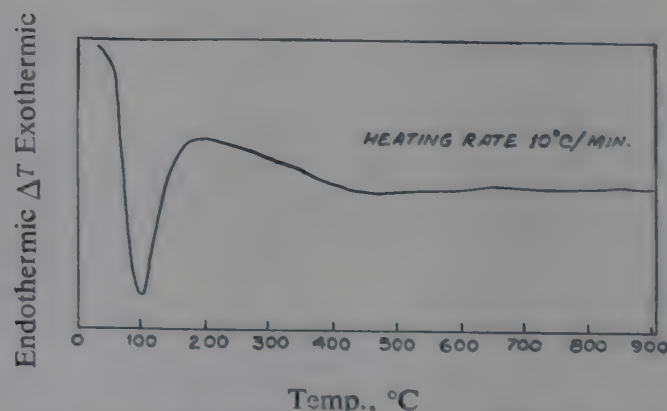


Fig. 4B—DTA Thermogram of a Copper Hydroxide Sample

Bulk Density (BD), Tablet Volume and Crushing Strength: The results on bulk density, tablet volume and crushing strength are presented Fig. 6. Bulk density of the catalyst dropped from 0.59 at 100°C to 0.52 g./cc at 200°C. It seemed that release of water from the pores at 200°C was responsible for the fall in bulk density because there was no shrinkage of the tablets. The crushing strength of the tablets increased regularly as the curing temperature increased but the other two parameters remained virtually unchanged in the range 200-400°C. At 500°C a distinct change occurred in all the three

properties. The change in crushing strength was particularly very large. It may be seen that for a rise from 600 to 800°C, where the bulk density and tablet volume changed by 25 and 50 per cent respectively, the strength of the tablet had gone up by 100 per cent. This drastic change in physical properties was reflected also in pore volume and surface area. (Fig. 2 and Table 1). A lower surface area and pore volume and higher BD appear to have contributed to higher mechanical strength.

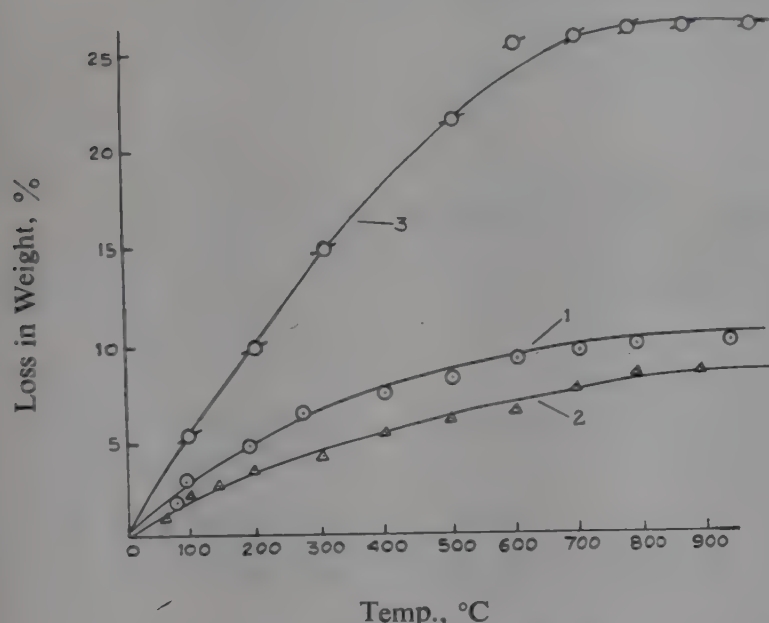


Fig. 5—TGA Thermograms

1=Kieselguhr, 2=Copper hydroxide, 3=Catalyst Sample

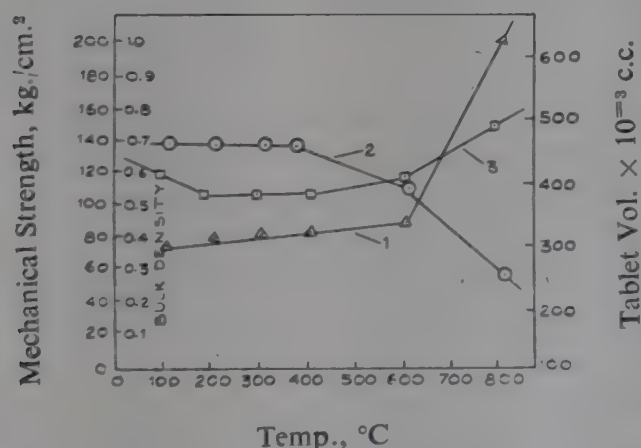


Fig. 6

1 = Mechanical Strength
2 = Tablet Volume
3 = Bulk Density

Activity: The effect of heat treatment on the activity of the catalyst is shown in Fig. 7. Activity was calculated as percentage conversion and also as specific activity (g. of acetaldehyde formed per unit surface of catalyst). It may be seen that the conversion was the highest with the samples cured at 200° and 300°C where the release of constitutional water was practically complete. There was marginal change in conversion with sample

cured at 400 and 600°C. Conversion dropped from 24.3 to 17.6 per cent as the curing temperature was increased to 800°C. If the activity is calculated as conversion per unit mass of catalyst instead of per unit volume, fall in activity will appear to be sharper. It showed that a copper catalyst can be used upto a temperature of 600°C without serious damage to activity.

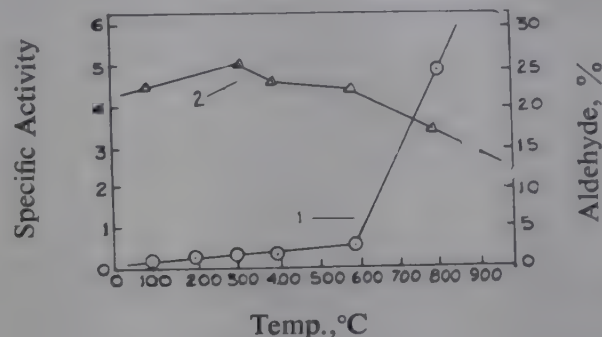


Fig. 7

1. Specific Activity 2. Aldehyde %

The specific activity of the catalyst (conversion per unit surface per hour) presented a contrast. It may be seen that the catalyst-I was least active when compared on the basis of specific activity and catalyst cured at 800°C was most active. This was just reverse to the activity calculated when on the basis of conversion per unit volume of catalyst. From the present observation in specific activity it was possible to draw a conclusion that active sites were not uniformly distributed on the surface. However, higher specific activity of the sintered catalyst was of little industrial advantage where space-time yield was the principal consideration. The copper catalyst for dehydrogenation of alcohol was generally used in the range 250-310°C. Therefore, for optimum activity the catalyst should be cured at 200-300°C. However, its activity is not likely to be seriously impaired in case the temperature shoots to 600°C during regeneration.

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TGA and DTA studies have been made on some nickel compounds of catalytic importance. Nickel hydroxide precipitated with ammonia decomposes at 290°C, while the same compound precipitated with sodium hydroxide decomposes at 325°C. Each of the two samples of nickel carbonate precipitated with ammonium carbonate and ammonium bicarbonate contained one molecule of water of crystallization. These precipitates release the lattice water around 160°C and decompose around 300°C. All these samples decompose in air to form nickel oxide containing excess oxygen. Nickel oxalate dihydrate loses lattice water at 210°C in a single step. It decomposes in air at 310°C forming finely divided nickel particles which then oxidize to give nickel oxide as the end-product. In the nitrogen atmosphere however, formation of nickel particles were confirmed by magnetic measurements. The observed magnetic moments at 25°C for nickel ions in these compounds lie within 3.1 ± 0.1 B.M., which support the proposed formulae of the precipitates derived on the basis of TGA data.

Thermal Decomposition Characteristics of Some Nickel Compounds of Catalytic Importance

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Nickel is the active component in a number of industrial catalysts. The role of d-orbital in catalysis is well known¹ and since nickel has an incompletely filled outermost d-orbital its capability towards surface adsorption is significant. The adsorption of reactants being one of the prerequisites of a catalyst and a fundamental aspect in catalysis, nickel occupies an eminent position among catalytic elements.

Different precipitants are generally used to precipitate nickel from its salt solutions to make supported catalysts and the commercial production procedure is based on the optimum performance obtained from experimental batches. Another important step in the catalyst manufacture is the curing of the precipitated mass. In this respect, the necessity of studying the thermal stabilities of precipitated masses can easily be recognized. Curing is sometimes accompanied with sintering which destroys the dispersion of the active ingredient. therefore, the curing temperature should be as low as possible, provided the other purposes of curing, like good mechanical strength, required phase composition, etc., are fulfilled. Although some of the compounds were studied^{2,3} earlier, it was considered important to re-examine the thermal decomposition characteristics of these compounds from catalytic

point of view. In the present study, nickel was precipitated by using ammonium hydroxide, sodium hydroxide, ammonium carbonate, ammonium bicarbonate and ammonium oxalate, and the thermal decomposition characteristics of the precipitated masses were studied by DTA and TGA techniques. The present studies on unsupported nickel precipitates may provide helpful guidance in the interpretations of the DTA and TGA thermograms of the same supported compounds in future.

Experimental

Preparation of the Samples: Nickel was precipitated from a 10 per cent (w/v) solution of A. R. nickel nitrate in distilled water, using saturated solutions of ammonium bicarbonate, ammonium carbonate, ammonium oxalate, sodium hydroxide and ammonium hydroxide. Nickel nitrate solution was constantly stirred during precipitation keeping it at 60°C. The precipitant solution was added at the rate of 1 ml./min. until the precipitation was complete. This mixture was kept at room temperature for 1 hr, then filtered and washed thoroughly to make the mass free of the precipitant. Filtered masses were dried at 120°C for 6 hours and kept in closed polythene bottles.

Thermogravimetric Analysis: A helical quartz spring balance⁴ housed in an all-glass enclosure was used for the thermogravimetric study. Weighed amount of sample was taken in a glass bucket and the temperature surrounding the sample was raised at the rate of 10°C/min. by means of a manually operated autotransformer which powered a nichrome wire-heater wound over the sample jacket. The rate of change of weight was observed through a micrometer microscope from the vertical displacement of an indicator. Sensitivity of the balance was 0.0148 mg. This instrument had a provision for studying the samples in controlled atmospheres or *in vacuo*. The present studies were mostly carried out in air.

Differential Thermal Analysis: A dual cell differential thermal analyser fabricated by the authors⁵ was used, the advantage being that two samples could be analysed simultaneously and the differential e.m.f.s could be recorded on a strip-chart single pen-recorder, which was converted to a dual channel by using an external transistorized converter. Chromel-alumel thermocouples made of 30 S.W.G. wires were used as detectors. Both the samples were put in the same furnace and heated by a manually operated autotransformer with 220 volts A. C. input. In all the cases, the reference material was finely powdered, α -Al₂O₃ ignited at 1300°C. Furnace temperature was raised at the rate of 10°C/min. All the DTA traces were confirmed by repeated runs.

Results and Discussion

Figs. 1A and 1B show the TGA and DTA curves for the precipitate obtained by using ammonia solution as the precipitant. It can be observed that the precipitate is a single component material, since its decomposition gives a single step at 290°C in the TGA curve and a single endothermic peak in the DTA curve at the same temperature. The elimination of moisture present in the precipitate appears as a minor endothermic hump in the DTA curve. It can be observed that even after the decomposition of nickel hydroxide at 290°C, there is a gradual loss in weight. Such a regular loss arises from the release of the excess oxygen, which nickel oxide contains, if prepared by low temperature decomposition of nickel compounds.

Figs. 2A and 2B show the TGA and DTA curves for the nickel hydroxide precipitate obtained by sodium hydroxide as the precipitating agent. Flame photometric estimation of sodium in the precipitate showed that it contained 0.55 per cent sodium, i.e. about 0.95 per cent sodium hydroxide. The TGA curve shows a two-step decomposition of the precipitate. The first step at 115°C

is due to the loss of moisture. Since sodium hydroxide is present in the mass as a minor phase, it is not showing any step in the TGA curve. It is evident from the TGA curve that nickel hydroxide precipitated by caustic soda decomposes at 325°C. This temperature is a little higher than the decomposition temperature of nickel hydroxide precipitated with ammonia solution.

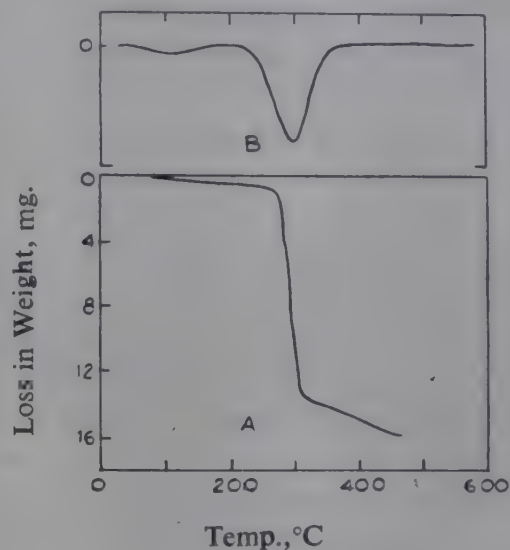


Fig. 1
A. TGA Thermograms of 31.5 mg. Nickel Hydroxide Precipitated by Ammonia
B. DTA Curve of the above sample

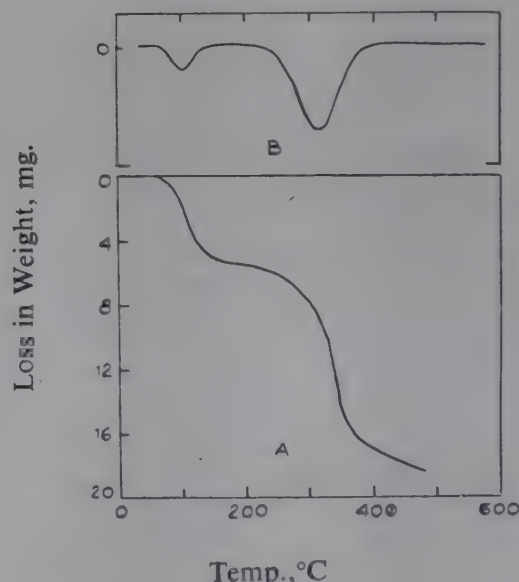


Fig 2
A. TGA Thermogram of of 56.2 mg Nickel Hydroxide Precipitated by NaOH
B. DTA Curve of the Above Sample

This temperature shift may occur due to a difference in the crystallite sizes of the two precipitates. In fact, a transmission microscope investigation revealed that the two precipitates are structurally different. The precipitate obtained by the action of ammonia is a flocculated amorphous powder, which is opaque through the microscope, while the precipitant caustic soda produced irregular shaped transparent crystals.

The difference in the decomposition temperatures is further confirmed from the DTA thermogram of the precipitate. The temperatures of both the peaks are in conformity with the TGA curve. The precipitate corresponds to the molecular formula $\text{Ni}(\text{OH})_2$ containing 10 per cent moisture.

In Figs. 3A and 3B, the TGA and DTA curves have been shown for the precipitate prepared from nickel nitrate and ammonium carbonate solutions. Both the curves indicate two distinct decomposition temperatures. The first step around 160°C seems to be due to the loss of water of crystallization, while the second step at 300°C is for the decomposition of nickel carbonate. The TGA curve of the precipitate is similar to that given by Duval³ for the nickel basic carbonate. He proposed the molecular formula of the basic salt as NiCO_3 , NiO or better Ni_2CO_4 nickel orthocarbonate. The present authors from the TGA data, found the precipitate to correspond the molecular formula $\text{NiCO}_3 \cdot \text{H}_2\text{O}$ but the mass picked up more water on ageing for 6 months to correspond the molecular formula $\text{NiCO}_3 \cdot 2\text{H}_2\text{O}$.

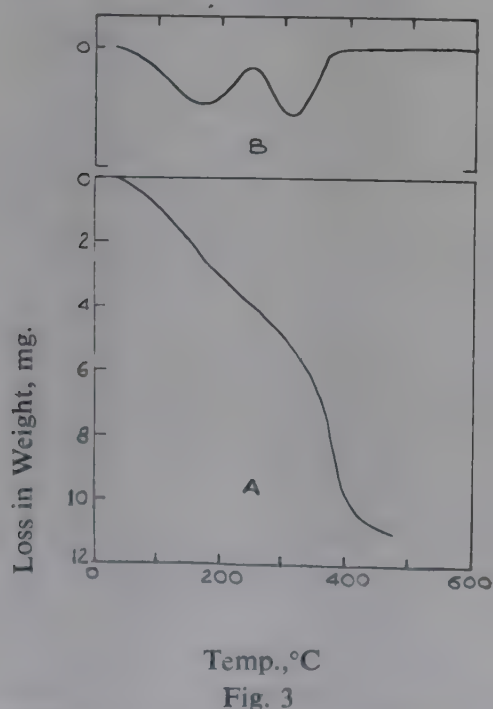


Fig. 3
A. TGA Thermogram of 26.0 mg. of Nickel Carbonate Monohydrate Precipitated by Ammonium Carbonate
B. DTA Curve of the Above Sample

Figs. 4A and 4B show the TGA and DTA traces of the precipitate obtained from ammonium bicarbonate and nickel nitrate solutions respectively. The precipitated mass shows thermal behaviour identical to that of the precipitate prepared with ammonium carbonate solution (Figs. 3A & 3B). That the dehydration process for this precipitate consists of two steps is evident from the TGA curve. The loss of moisture is complete

at 115°C and then release of water of crystallisation starts. The total water present in the precipitate corresponds to one molecule of water of crystallization. It can be observed from Fig. 4A that about 40 per cent of the total water is present as loosely-bound moisture and the rest is lattice water. The decomposition product of this precipitate contains a considerable amount of excess oxygen can be observed in the TGA curve, since constancy in weight was not observed upto 450°C . In a similar study, Deville⁷ obtained the hexahydrate $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ by precipitating nickel from its nitrate by the action of sodium bicarbonate or ammonium bicarbonate.

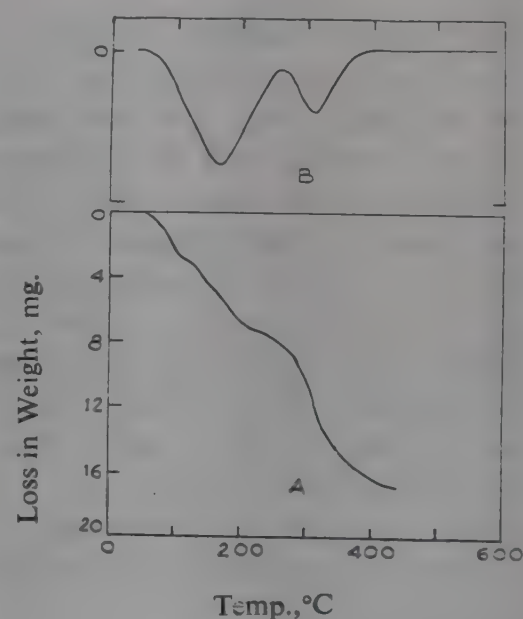


Fig 4
A. TGA Thermogram of 51.7 mg. Nickel Carbonate Monohydrate Precipitated by Ammonium Bicarbonate
B. DTA Curve of the Above Sample

Therefore, it seems that when nickel is precipitated either with ammonium carbonate or ammonium bicarbonate from its nitrate solution at 60°C gives a hydrated nickel carbonate.

The nickel oxalate dihydrate is probably the most widely studied nickel compound. Many authors have reported⁸⁻¹² the kinetics of decomposition of the compound in air or in vacuum. The present report is restricted to the interpretations of the TGA and DTA curves of this compound. The thermal analyses of the precipitate prepared from ammonium oxalate and nickel nitrate solutions are shown in Figs. 5A and 5B. The TGA curve comprises two stages of weight-loss. The traces of moisture are driven off first within 100°C , which is then followed by a loss of two molecules of water of crystallization at 210°C . The anhydrous nickel oxalate then decomposes at 310°C . An examination of the DTA curve-I shows that the expulsion of the water

of crystallisation and then decomposition of the anhydrous nickel oxalate is followed by a slow process of aerial oxidation of the finely divided nickel particles formed earlier, to give the hump type large exothermic peak. This part of the process is very similar to the decomposition of nickel dimethylglyoxime complex⁵. The thermomagnetic behaviour of the end-product was studied, which showed that nickel oxide is formed at the end of the decomposition. The curve-II (Fig. 5B) is the DTA thermogram for the compound in an atmosphere of nitrogen. The absence of the exothermic hump type peak in this case, points out that finely divided nickel would be the end product. In fact, the magnetic behaviour of the end product was found to correspond to that of metallic nickel. Thus the differential

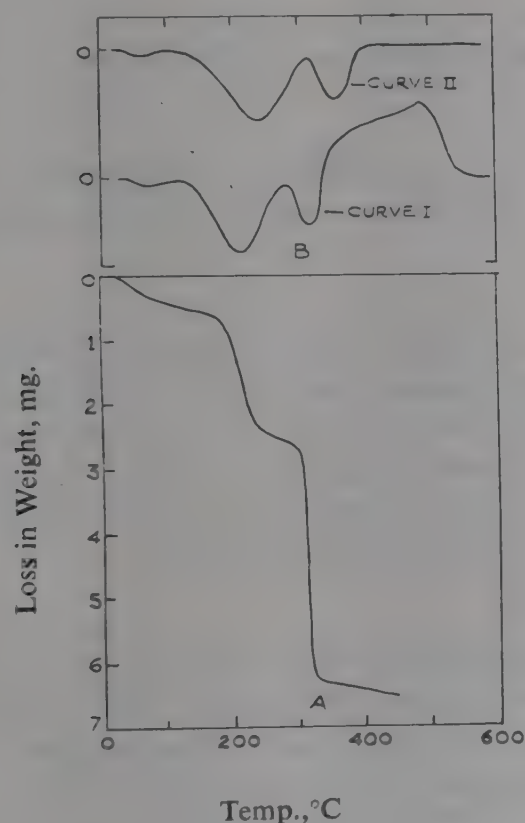
thermal analysis of the compound can explain the probable reaction mechanism of the decomposition of nickel oxalate dihydrate. This is also corroborated by the magnetic data.

The molecular formulae of the precipitates derived on the basis of the TGA data were used to calculate the magnetic moments of the Ni ions in these compounds. The observed magnetic moments at 25°C for a Ni ion in these five compounds lie within 3.1 ± 0.1 B.M. These values further support the proposed formulae of the precipitates.

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Temp., °C

Fig. 5

- A. TGA Theragram of 10.4 mg. of Nickel Oxalate Dihydrate Precipitated by Ammonium Oxalate
 B. DTA Curves of the Above Sample in Nitrogen (Curve II) and air (Curve I)

The stoichiometric equations proposed by Benson and Boudart, and Mears and Hansford for the gas chemisorption and subsequent titration over the alumina-supported platinum surfaces were reinvestigated. Ratios of 1:1:3 of HC:OC:HT were found to conform with the present authors results for a catalyst having a high degree of metal dispersion. In cases of catalysts sintered at higher temperatures, this ratio does not hold good. In fact nearly constant values of oxygen chemisorption were observed as against the regularly decreasing hydrogen uptake values with increasing sintering.

In spite of the excellent repeatability of the titrations, it does not appear proper to recommend the use of oxygen chemisorption data for obtaining metal area and dispersion.

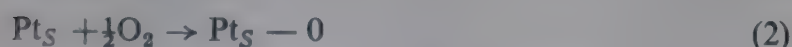
An Investigation of the Nature of Oxygen-Hydrogen Titration of Supported Platinum Catalysts

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Introduction

Studies on the active platinum area and metal dispersion over supports, using chemisorption of hydrogen and carbon monoxide have been widely reported in literature¹⁻⁴. Based on the stoichiometry suggested by Gruber³, Benson and Boudart⁵ proposed a new method for the measurement of the platinum surface area. The method involves the titration of oxygen chemisorbed on the metal surface with gaseous hydrogen. They proposed the following stoichiometries:



The above equations and the method were re-examined by Mears and Hansford⁶. These authors maintain that a more appropriate stoichiometry at 25°C and a pressure of about 10 torr would be as follows:



On the other hand, Wilson and Hall⁷ observe that only the hydrogen chemisorption data are reliable and in no case the oxygen chemisorption or oxygen-hydrogen titration can be regarded as a measure of the available platinum area.

The present work deals with the verification of the uncertainties pointed out above, using an alumina-supported platinum catalyst with surface modified by sintering to various extents. An attempt has been made to explain the discrepancies observed in the oxygen-hydrogen ratios during the titration.

Experimental

The catalyst used in this work was of a commercial variety with a platinum content of 0.18% supported on γ -alumina. A conventional volumetric apparatus was used to measure the chemisorption of gases at room temperature. After reduction in a stream of purified hydrogen the outgassing was carried out at 10^{-5} torr and at 500°C for 16 hours. The hydrogen chemisorption was carried out at room temperature and upto a pressure of 200 torr. The amounts of the chemisorbed gases were obtained from the intercepts of the isotherms by extrapolation to zero pressure^{6,7,9}.

Two sets of chemisorption and titration experiments were carried out. In one group of experiments samples of the original catalyst were reduced in an atmosphere of hydrogen at 500, 600, 700 and 770°C. After hydrogen chemisorption, the sample in each case was evacuated at 10^{-5} torr and 500°C for 2 hours. The oxygen chemisorption and its titration by hydrogen were done on the clean surfaces thus obtained.

In another set of experiments a sample reduced at 500°C for 4 hours was evacuated at the same temperature for 16 hours. The following titration cycles were followed on this sample :



In these experiments the sample was evacuated at 10^{-5} torr and at 30°C for 45 minutes after each step of the chemisorption and titration cycle.

Results and Discussion

Table-1 shows the results of chemisorption and titration experiments for the samples sintered in hydrogen at 500, 600, 700 and 770°C. The reduction in the metal area as observed here, has been previously reported^{2,3,7} under similar conditions. With the increasing temperature, the hydrogen uptake was found to drop steadily reflecting a regular decrease in platinum surface area ; the oxygen chemisorption however remained more or less constant. The HC : OC : HT ratios were very nearly equal to 1:1:3 in the case of only one catalyst sample with H/Pt = 0.8. The departure from this becomes prominent with the decrease in H/Pt ratio. Wilson and Hall⁷ have shown that this ratio shifted from 2:1:4 to 1:1:3 with the increasing-sintering between 500° and 800°C. In the present study, however, the ratio 2:1:4 could not be obtained for any of the samples.

TABLE 1—VOLUMES CHEMISORBED AT NTP FOR THE SINTERED CATALYSTS

(Ambient temperature=30° C; Wt. of the Catalyst=7 g.)

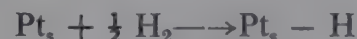
Temp. °C	Time of Red. hr	H ₂ -chem. ml.	O ₂ -chem. ml.	H ₂ -titr ml.	H/Pt Ratio
500	2	0.58	0.51	1.56	0.80
600	15	0.34	0.40	1.10	0.47
700	15	0.22	0.39	0.98	0.30
770	15	0.10	0.42	0.90	0.14

The nearly constant values of the oxygen chemisorption volume point out the inadequacy of the oxygen chemisorption or O₂-titration as a method for the measurement of platinum metal area. It appears that whereas hydrogen is absorbed only on the surface, oxygen is able to react with the bulk Pt-atoms also to some extent even at room temperature due to the stronger affinity of oxygen for the oxide bond formation. The extent of the bulk oxidation would, however, be governed by the reaction temperature, partial pressures of oxygen and the duration of exposure of the metal to oxygen pressures.

Gruber³ has reported similar bulk oxidation of the metal at 300°C, while in the present case it appears that such a possibility can not be ruled out even at room temperature. If the metal dispersion is so high, that all the platinum is accessible on the surface, then the difference between the uptakes of hydrogen and oxygen can not become so significant. However, for catalysts having relatively fewer platinum atoms exposed on the surface, the oxygen uptake is more than hydrogen as in the case of catalysts with H/Pt=0.14 and 0.30.

Though the hydrogen chemisorption values are always consistent and are widely recommended for the measurement of platinum area, recent studies on the types of hydrogen bonding^{8,9} on the Pt sites raise doubts regarding the use of the ratio H/Pt_s = 1 for this purpose. Aben *et al*⁹, from their studies on the TPD of chemisorbed hydrogen on alumina-supported platinum catalysts, showed that the platinum surface after a given heat treatment in hydrogen is very much heterogeneous. The treatment causes the changes in the ratio of the various sites contributing to the average H/Pt ratio.

Thus, an increase in the δ -form of sites ($\text{Pt} \begin{smallmatrix} \text{H} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Pt}$) due to sintering or otherwise would affect the stoichiometry assumed in the present case :



It therefore appears necessary to evaluate the exact ratios of the individual sites present for hydrogen chemisorption to be useful for the determination of the correct H/Pt ratio.

The chemisorption and titration cycles for the catalyst samples sintered at 500°C and 770°C were carried out in the following sequences : (a) O₂ — H₂ — O₂ and (ii) H₂ — O₂ — H₂

The results are summarised in Table II. For the first sequence of the experiments, the volume of oxygen chemisorbed is found to be 0.55 ml. The first hydrogen titration over this yields a value of 1.58 ml. This comprises the volume of hydrogen required to convert 0.55 ml. of oxygen into water and the amount required to cover the bared surface platinum atoms. Thus the amount of hydrogen covering the platinum sites works out to 0.48 ml. This is close to the value of 0.44 ml. found for the hydrogen adsorption on the clean catalyst surface. In the second cycle of this sequence, the volume of oxygen consumed is 0.77 ml. If it is assumed, that the same value of oxygen (0.55 ml.) is adsorbed as in the first oxygen chemisorption, the amount of oxygen

TABLE 2—VOLUME OF GASES CONSUMED DURING CHEMISORPTION AND TITRATION CYCLES AT NTP
(Ambient temperature=30° C, Sample Weight=7.0 g.)

Sequence	Reduction temp. °C	O ₂ -chem. ml.	H ₂ -tit. I ml.	O ₂ -tit.II ml.	H ₂ -tit.III ml.	O ₂ -tit.IV
O ₂ -H ₂ -O ₂	500	0.55	1.58	0.77	1.54	0.76
	770	0.42	1.00	—	0.92	—
		H ₂ -chem. ml.	O ₂ -tit.I ml.	H ₂ -tit.II ml.	O ₂ -tit.III ml.	H ₂ -ti.IV ml.
H ₂ -O ₂ -H ₂	500	0.44	0.75	1.66	0.79	1.64
	770	0.10	0.51	0.90	0.46	—

required for the formation of water would be expected to be 0.22 ml. which is equivalent to 0.44 ml. of hydrogen. This again is very close to the previously obtained value of 0.48 ml. of hydrogen on the clean surface. The third and fourth cycles of the experiment also bear the same relationships as found for the earlier two cycles within experimental errors. A similar relationship holds for the catalyst sintered at 770°C also.

The cycles in the second sequence, i.e. H₂ — O₂ — H₂ .. also show a similar relationship for both the catalysts. The results lead to the following conclusions : (i) Titration reactions in both the sequences are quantitative and it is immaterial which gas (H₂ or O₂) is chemisorbed first (ii) The consistency observed in the results for all the cycles and sequences shows the excellent repeatability of the experiments. (iii) The water produced during the titration does not appear to interfere with the next cycle of titration which shows that the water formed is probably physisorbed on the support because of its strong hydrophilic nature. Basset *et al*¹⁰. arrived at this conclusion from the low heats of adsorption (18 K cal/mole) for water on platinum-alumina system during titration.

On the basis of the results shown in Tables 1 and II and from the above discussions, it is found that the stoichiometric ratios between the hydrogen and oxygen

chemisorption on the platinum surface do not follow any set rule. As pointed out the stoichiometries of equations 1, 2 and 3 hold good only in the case of the catalyst with a high degree of dispersion, e.g., H/Pt=0.8 At present there appears to be no definite explanation for the discrepancy. However, Basset *et al*¹⁰ summed up several possible factors responsible for the anomaly : differences in the out-gassing procedure, change in the crystallite sizes, changes in the degree of water content of the support, and the complex behaviour of hydrogen towards platinum could be major difficulties in explaining the discrepancy.

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Attempts were made to produce mutations in some vegetatively propagated ornamentals by acute and chronic gamma irradiation. Rooted cuttings of *Chrysanthemums* and dormant bulbs of Dahlias were exposed to 1.5, 2.5, 3.5 and 2.0, 3.0 kR of acute doses respectively. In chronic irradiation, potted plants of *Bougainvillea*, *Hibiscus*, *Allamanda*, *Achania*, *Jasminum*, *Chrysanthemum* were exposed to several dose rates at different isodose arcs in the gamma field. Chronically exposed materials showed decreased growth with increased doses besides various physiological abnormalities, like fused growth, bifurcated leaf and midrib, narrow leathery leaf, budless growth, etc. With acute irradiation a total of four flower colour mutants in Angel Belle, Pride of Midford, R. C. Pinch and Pink Cloud cultivars of *Chrysanthemum* and that of three in Croydon Monarch and Black Out cultivars of *Dahlia* were isolated. In chronic irradiation, two flower form and one flower colour mutants have been spotted out in Alipore Beauty, Mutant Alipore Beauty and Syriacus Pink Double cultivars of *Hibiscus*. The *Hibiscus* mutants were isolated at dose rates of 32, 48, 32 R/hr with total doses of 17.4, 10.6 and 22.2 kR respectively. Similarly, one flower colour mutant was isolated in Ajina Purple cultivar of *Chrysanthemum* at 24 R/hr with an accumulated dose of 14.5 kR. These mutants are being vegetatively multiplied and some of them have already been stabilized as pure forms.

Induction of Somatic Mutations in some Vegetatively Propagated Ornamentals by Gamma Irradiation

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Introduction

Spontaneous mutations have played a significant role in the evolutionary history of flowering and ornamental plants. Considerable success has also been achieved in inducing mutations in a number of ornamentals by several workers¹⁻¹³. In India not much work has so far been done for the improvement of ornamentals with the aid of this potent genetic tool. The highly heterozygous and vegetatively propagated ornamentals are very suitable test materials for experimental mutagenesis. Nevertheless, with the increasing importance of floriculture industry in India and also greater availability of irradiation facilities at various institutions, more attempts are now being made for improvement of ornamentals by induced mutations. Khoshoo¹⁴, while discussing the genetical improvement of ornamentals, and Bose¹⁵, reviewing the work on ornamentals in India over the last two decades, clearly emphasized the importance of induced mutation method in ornamental improvement programme. Recently, Das *et al*¹⁶ reviewed the work done in induced mutations in some important ornamentals and brought out some of the problems confronted in such projects. While in some of

the earlier publications the present authors reported the results of induced mutations in *Hibiscus*, *Chrysanthemum*, *Iresine*, *Acalypha*^{12,13} the present paper, reports the results with some more materials.

Materials and Methods

The Co⁶⁰ field installation (gamma field) of the Planning and Development Division was utilized for irradiation treatments for both acute and chronic exposure of the materials. Rooted cuttings of pot grown perennial *Chrysanthemums* and dormant bulbs (fasciculated roots) of large-sized *Dahlias* were given acute exposure with doses 1.5, 2.5 and 3.5 kR in the former and 2.0 and 3.0 kR in the latter material. Twenty rooted cuttings of *Chrysanthemums* and 5 bulbs of *Dahlias* were included in each treatment with equal number of controls (OkR). In chronic irradiation, however, potted plants of *Bougainvillea*, *Hibiscus*, *Acalypha* and *Chrysanthemum* were exposed. The pots were positioned radially in the exposure field at different isodose arcs from the source. The source was operated during the night for an average of 9 hr/day. Growth data of the chronically exposed materials were taken at regular

intervals and growth abnormalities were also recorded from time to time. The experiments described herein were carried out during 1971-73 with the object of isolating some desirable mutations.

Post-Irradiation Treatment of the Materials

Since post-irradiation treatment of materials is one of the decisive factors for optimal results in such experiments, more efforts were made to increase the chances of mutated cell to take part in growth as fully as possible. As soon as the irradiated *Chrysanthemum* cuttings (in acute irradiation) started to grow the terminal growing point was pinched off to form side shoots from axils. Similarly, cuttings from the irradiated bulbs of *Dahlias* were made from top region gradually to down below so as to force growth from lower axils. However, in chronically exposed materials, no sooner any change was noticed, all the normal growths were removed, thus allowing the changed cells to multiply quicker and express further. This helps the mutated cells to grow into a group of cells, a sector and finally to a completely changed shoot by minimizing diplontic or intrasomatic selection. As soon as any sizeable amount of changed growth was established cuttings were made for perpetuation and carry over of the material to the next vegetative generation.

Results and Discussion

Effect of Irradiation on Growth and Morphology: Working with a number of ornamentals, it was found that with the increase in doses, there was, in general, a corresponding decrease in growth (Table 1). Although growth data were taken at monthly intervals, data at the end of 5 months are summed up in Table 1. The

maximum retardation of growth was recorded at the highest dose, i.e. 342.5 R/hr followed by that in 85.5 R/hr and so on. None of the plants at higher doses could withstand exposure for the whole period of investigation (5 months) and hence, they were removed from the exposure field. Interestingly, however, at lower doses (8.5, 12.0 R/hr) there was an increase in growth, i.e. stimulation was recorded in *Bougainvillea*, *Jasminum* and *Syriacus Hibiscus* (Table 1). This stimulation was noticed at every month while taking observations. Besides the effect of radiation on growth, various physiological anomalies (primary biological effects), like fused growth, bifurcated leaf and midrib, narrow leathery leaf, budles growth, etc. were recorded.

Induced Mutants: The flower colour and flower form mutants isolated in different cultivars of *Chrysanthemum*, *Dahlia* and *Hibiscus* either by acute or chronic irradiation are presented in Table 2. It is seen from the table that both whole plant mutations and chimeric forms were observed. In order to recover totally mutated plants from the induced chimeras (mixochimera), vegetative propagation (cutting) was practised to see whether they breed true to type in the next vegetative generation (VM) and compare with the original stock. In 1972 although only one whole plant mutation was spotted out in the Pride of Midford cultivar of *Chrysanthemum*, in 1973 a number of whole plant mutations were isolated from mass cuttings made from the visibly unaffected treated plants. This clearly demonstrates that the changes which remain latent in chimeric form in vegetative tissue in the irradiated generation can be exposed in the next generation if a thorough and an effective propagation method is adopted.

TABLE 1—EFFECT OF CHRONIC GAMMA IRRADIATION ON GROWTH OF SOME ORNAMENTALS
(Percentage inhibition/acceleration over control—after 5 months' exposure)

Dose Rate, R/hr	Material						
	Bougainvillea			Hibiscus		Jasminum	Ixora
	Mrs. H.C. Buck	Scarlet Queen	Mrs. Fraser	Alipore Beauty	Syriacus Maure Double	Auriculatum	singaporensis
5.0	22.17	22.23	—	10.75	9.30	40.28	14.33
8.5	(+)57.47	(+)59.23	—	13.32	(+)4.36	(+)34.62	17.17
12.0	(+)23.76	(+)7.45	(+)31.70	12.95	25.64	(+)10.25	24.76
18.5	64.58	51.23	18.56	22.38	38.26	63.75	34.94
25.0	104.35	147.28	73.44	36.56	62.85	54.79	42.55
32.0	146.50	258.37	123.37	48.29	59.42	75.57	40.42
48.0	197.58	Ceased after 4 months	107.78	45.47	74.36	120.26	58.35
85.5	Ceased after 4 months	Ceased after 2 months	226.93	Ceased after 4 months	84.36	154.64	Ceased after 4 months
342.5	Ceased after 4 months	Ceased after 1 month	Ceased after 3 months	Ceased after 2 months	Ceased after 2 months		Ceased after 1 month

(+) indicates stimulation of growth; others indicate inhibition of growth.

TABLE 2—MUTANTS IN SOME ORNAMENTALS AFTER ACUTE AND CHRONIC GAMMA IRRADIATION

Material	Induced Change		Type of Exposure		Whole Plant Mutation/ Chimeric
	Flower Colour	Flower from	Acute	Chronic	
I. <i>Chrysanthemum</i> :					
1. Pride of Midford (Deep Pink)	Brown orange	—	1.5 kR	—	Whole Plant
2. Angle Delle (Light pink)	Light yellow	—	2.5 kR	—	Whole Plant
3. R. C. Pinch (Deep pink)	Light orange-brown	—	2.5 kR	—	Chimeric
4. Pink Cloud (Light pink)	Light yellow	—	2.5 kR	—	Chimeric
5. Agina Purple (Purplish pink)	White	—	—	14.5 kR (24 R/hr)	Chimeric
II. <i>Dahlia</i> :					
6. Croydon Monarch (Red)	Violet red	—	2.0 kR	—	Whole Plant
7. Black Out (Deep red)	Pink	—	2.0 kR	—	Whole Plant
III. <i>Hibiscus</i> :					
8. Syriacus Double (Deep mauve)	White	—		22.2 kR (32 R/hr)	Chimeric
9. Alipore Beauty (Carmine red)	—	Single		17.4 kR (32 R/hr)	Chimeric
10. Mutant Alipore Beauty (Double, Deep red)	—	Single		10.6 kR (48 R/hr)	Chimeric

It was also found that only the pink-flowering varieties of *Chrysanthemum* showed positive response to irradiation. This is because the pink colour in *Chrysanthemum* is based on a number of dominant genes. Broertjes⁷ also got the maximum number of mutations predominantly with the pink-flowering *Chrysanthemum*.

Table 2 also shows that out of 10 mutants isolated in various ornamentals, only 2 were of flower form (in *Hibiscus*) and the rest were in respect of flower colour. One of the authors (PKD) of this paper had already reported flower colour and flower form mutations in Alipore Beauty which resulted in deep red and semi-double mutants. In the present study, again Alipore Beauty (Carmine red, double) and mutant Alipore Beauty (deep red, double) were exposed and single forms both in Alipore Beauty and Mutant Alipore Beauty were obtained. Therefore, from double form of *Hibiscus* the authors could isolate both semi-double and single forms. The range of mutations in Alipore Beauty cultivar of *Hibiscus* is represented below:

	<i>Mutant</i> (Carmine red, Single)	
<i>Alipore Beauty</i> (Carmine red, Double)	<i>Mutant</i> (Deep red, Double)	<i>Mutant</i> (Deep red, Single)
	<i>Mutant</i> (Deep red, Semi-double)	

It is, thus, seen that the changes for flower colour and flower form are due to independent events and the pleiotropic effect is ruled out since changed colour is not accompanied with changed flower forms, hence is also not a case of multimutation. All the mutants are being vegetatively multiplied and some of them have established as pure forms through one or two vegetative generations.

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The compatibility and effectiveness of different urea-insecticide mixtures were studied under field and laboratory conditions on various insect pests. Foliar application of insecticides, like endrin, diazinon, malathion, phosphamidon, thiometon and endosulfan, either alone at the concentration of 0.05 per cent or mixed with 2 per cent urea reduced the leaf hopper population considerably in brinjal (vgr. Ramnagar) under field condition. A significant decrease in the brinjal fruit borer infestation was observed in all the treatments with insecticides either alone or with urea than with urea or control without insecticides. The yield increase was also found to be significant in all the treatments with urea with or without insecticides than control, with maximum in urea-endrin and urea-phosphamidon.

No appreciable change in the efficacy of the insecticides was observed under laboratory condition with *Avlacophora foveicollis* Lucas as a test insect in respect of residual toxicity and fumigation action. However, endrin with urea proved to be more effective than other insecticides under test.

Studies on the Compatibility and Effectiveness of Different Urea-Insecticide Mixtures

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In usual practice a separate schedule for application of fertilizer and pesticides is recommended for each crop, which obviously involves higher cost. A considerable yield increase was obtained by several workers¹⁻³ in different crops with the application of fertilizers mixed with pesticides. It was, therefore, considered of interest to utilize fertilizer-insecticide combination as a foliar spray on a remunerative crop, like brinjal, where a large quantity of fertilizer as well as pesticides are usually recommended to get a pest-free high-yielding crop.

EXPERIMENTAL

Field Study: A replicated field trial with randomized block design was conducted in the farm of the Agricultural Research Centre, Sindri in 1969 with Ramnagar Variety of brinjal. The details of the treatment combinations are listed in Table 1. A basal dose of 40 kg. nitrogen, 40 kg. phosphate (P_2O_5) and 40 kg potash (K_2O) in the form of urea, single superphosphate and muriate of potash respectively was applied during soil preparation. Another dose of 40 kg./ha of nitrogen in the form of urea was applied in four equal split applications as foliar spray in a set of treatments at fortnightly interval starting from 25 days after transplantation. The concentrations of urea and insecticides

were maintained at about 2.2 and 0.05 per cent active ingredient respectively in the spray mixture. Each plot received 1.5 litres of spray mixture which was equal to 1000 l./ha. There were altogether 14 treatment combinations with three replications. The number of leaf hoppers/plant/treatment were counted early in the morning before and after treatment application. the borer infested fruits were separated from total harvest at each picking from each plot in order to get the percentage borer infestation.

Laboratory Investigation with Aulacophora Beetles for Residual Action: The emulsifiable concentrates of the insecticides, viz. endrin, phosphamidon and endosulfan, were diluted at 0.05 per cent active ingredients with water and sprayed separately with or without 1 per cent urea on 15 days old potted plants of watermelon with an atomizer to obtain a uniform application for all cases. Adult red pumpkin beetles were collected from the field early in the morning and kept without food for 6 hours in a glass jar. 10 such beetles were then released in each pot having sprayed plants caged in glass chimneys at intervals of 1, 24, 48 and 72 hours. The upper open end of the chimney was covered with muslin cloth. The exposure period was kept 24 hours after which the mortality count of the insects was

taken. The percentage mortality for each treatment at different periods were then converted by Abbott's formula⁴ and the 'PT' index was calculated.

Fumigation Action: In another set of experiments, the glass jars (7 cm. diam. and 10 cm. height) containing 3 ml. of the 0.05 per cent of the active concentration of the insecticides, like endrin, phosphamidon, endosulfan, lindane, malathion, fenitrothion, and urea-insecticides mixtures separately were covered with muslin cloth on which the glass chimneys were placed upside down to fix on the upper end of the jar. Each chimney was provided with one tender pumpkin leaf and 10 adult red pumpkin beetles. After 24 hours, the mortality of the beetles inside the chimney was counted.

RESULTS AND DISCUSSION

Decrease in Leaf Hopper Population

Table 1 shows a considerable decrease in leaf hopper population in all treatments, where insecticides were applied either alone or mixed with urea after first application. In all cases, more than 90 per cent mortality was observed with maximum in urea+thiometon (97.3 per cent) closely followed by phosphamidon (96.3 per cent), urea+phosphamidon (96.2 per cent) and thiometon (96.1 per cent). An increase of 4.7 per cent of leaf hopper population was observed in control (water spray) after first application of the insecticides.

TABLE 1—CONTROL OF LEAF HOPPER POPULATION IN DIFFERENT TREATMENTS

Treatment	Mean No. of Leaf Hopper Population before 1st Spraying, per Plant	Control of Leaf Hopper Population after 1st Spraying, %	Mean No. of Leaf Hopper Population before 2nd Spraying, per plant	Control of Leaf Hopper Population after 2nd Spraying, %
Endrin	16.3	93.8	38.0	93.9
Urea + Endrin	13.6	88.3	56.0	92.8
Diazinon	14.6	95.9	29.6	95.6
Urea + Diazinon	15.6	93.5	30.6	94.7
Malathion	13.0	92.3	38.0	97.3
Urea + Malathion	8.0	91.7	49.7	96.7
Phosphamidon	18.0	96.3	12.6	95.2
Urea + Phosphamidon	17.6	96.2	20.3	95.1
Thiometon	17.3	96.1	13.6	88.2
Urea + Thiometon	12.6	97.3	20.6	95.1
Endosulfan	8.0	91.7	18.0	94.4
Urea + Endosulfan	16.3	91.8	28.3	94.1
Urea	12.6	7.8*	59.3	11.7*
Control	14.0	4.7*	61.0	28.9*

* Percentage increase in leaf hopper population.

The decrease of the leaf hopper population after second application was also considerable. The highest control was observed in malathion (97.3 per cent) followed by urea+malathion (96.7 per cent), diazinon (95.3 per cent), phosphamidon (95.2 per cent), urea+phosphamidon (95.1 per cent) and urea+thiometon (95.1 per cent). An increase of 11.7 and 28.9 per cent in the leaf hopper population was observed in urea and control respectively after second application.

Infestation by Brinjal Borer

It is evident from Table 2 that the minimum infestation was in phosphamidon, closely followed by thiometon and urea+phosphamidon and has no significant variation with endosulfan, urea+endosulfan, urea+ diazinon, urea+malathion, urea+thiometon and endrin. The highest percentage of infestation was observed in the control plots, closely followed by urea, and differs significantly with all other treatments.

TABLE 2—BORER INFESTATION AND MEAN YIELD IN DIFFERENT TREATMENTS

Treatment	Fruit Borer Infestation, %	Yield, kg./ha.	Increase in Yield over Control, %
Endrin	6.74	21613	92.1
Urea + Endrin	7.59	30233	168.7
Diazinon	7.26	15267	35.7
Urea + Diazinon	5.82	17220	53.0
Malathion	9.13	15860	40.9
Urea + Malathion	5.83	25987	130.9
Phosphamidon	2.73	16293	44.8
Urea + Phosphamidon	4.04	29647	163.4
Thiometon	3.75	16933	50.5
Urea + Thiometon	6.10	21520	91.2
Endosulfan	4.92	20053	78.2
Urea + Endosulfan	5.11	26680	137.1
Urea	22.69	18207	61.8
Control	23.26	11253	
C.D. at 5%	4.22	4443	

Laboratory Investigation

Residual Toxicity: All treatments resulted in more than 86 per cent mortality with the highest of 100 per cent in urea+endrin, phosphamidon, urea+phosphamidon and endosulfan, when the beetles were exposed to one hour old spray residues. With 72 hours spray residues however, most of the insecticides lost appreciable toxicity, either alone or in combination, with urea and endosulfan and urea+endosulfan became completely ineffective. By taking 'PT' values as index of

relative toxicity, the performance of insecticides was in the following order : urea+Endrin>Phosphamidon and urea+phosphamidon>Endrin>Endosulfan>urea+Endosulfan (Table 3).

TABLE 3—TOXICITY OF SOME INSECTICIDES AND UREA-INSECTICIDE MIXTURES TO ADULT *Aulacophora* BEETLES

Treatment	Corrected Mortality, %				‘PT’ Index
	Age of the Spray Residue				
	1 hour	24 hours	48 hours	72 hours	
Endrin	86.6	86.6	76.6	10.0	194.7
Urea + Endrin	100.0	90.0	76.6	10.0	207.3
Phosphamidon	100.0	90.0	70.0	10.0	202.5
Urea + Phosphami- don	100.0	93.3	63.0	13.3	202.5
Endosulfan	100.0	80.0	43.3	3.3	169.2
Urea + Endosulfan	86.0	76.6	46.6	0.0	157.2

For Fumigation Action: A perusal of the Table 4 will show that significant variation exists in the mortality among the treatments. The maximum mortality was obtained in lindane and urea+lindane and differ significantly from all other treatments. The minimum was obtained in fenitrothion, closely followed by urea+fenitrothion, which differ significantly from all other treatments. Significant variation was not observed between the two forms of insecticides, viz. insecticides and insecticide-urea mixture. No mortality was observed where the plants were sprayed only with urea as well as in the control.

These experiments clearly indicate that urea has no adverse effect on the insecticides on trial. On the con-

trary a slight synergistic effect which has been observed in certain insecticides needs further investigation.

TABLE 4—TOXICITY OF SOME INSECTICIDES AND UREA-INSECTICIDE MIXTURES TO ADULT, *Aulacophora* BEETLES

Treatments	Mortality*, %
Endrin	50.89
Urea+Endrin	60.11
Lindane	90.00
Urea + Lindane	90.00
Malathion	67.50
Urea + Malathion	60.11
Phosphamidon	53.78
Urea + Phosphamidon	56.79
Endosulfan	45.00
Urea + Endosulfan	42.11
Fenitrothion	29.92
Urea + Fenitrothion	32.90
C.D. at 5%	10.93

* Angular transformed value.

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In order to find out the relationship between nitrogen status of the host plant and incidence of pests in brinjal (Var. Pusa purple Long), a replicated field trial was undertaken with eight levels of nitrogen in a randomized block design. The leaf hopper population at different ages of the host, fruit borer damage, yield, moisture and nitrogen percentage of the plants were recorded and analysed.

An increase in the application of nitrogen in soil resulted significantly higher nitrogen content of the host plant and consequently more leaf hopper population in all the five stages of growth. The minimum average population was observed in N_0 followed by N_{20} and the maximum was in N_{120} . The treatment effect was found to be significant upto 1 per cent level. But no significant relationship was obtained between the fruit borer damage and the levels of nitrogen application. Maximum fruit yield was obtained in N_{120} , which was as high as 26.89 tonnes. The minimum fruit yield was, however, obtained in N_0 level.

Effect of Graded Doses of Nitrogen on the Pest Incidence and Yield of Brinjal Under Field Condition

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The relationship between nitrogen status of the host plants and pest attack has been demonstrated by several authors¹⁻⁵. Even then a sweeping generalization cannot be made in this respect because of the extreme differences in the nutritional requirements of the crop plants, soil type and diversity in the behaviour of insect pests. As a matter of fact, Kundu and Pant⁶ could not find any appreciable effect on the fecundity and longevity of aphids in mustard with varying amount of nitrogen in the host plant. In the case of brinjal, a high nitrogen consuming crop, cultivation is severely handicapped by the attack of several insect pests. But very little work has been done on the effect of graded doses of nitrogen to the soil. This aspect has been studied in the experiments reported in this paper.

Materials and Method

The field was prepared with eight cart-loads of F.Y.M. per hectare and applied uniformly. Graded doses of nitrogen, viz. 20, 40, 60, 80, 100, 120 and 140 kg./ha. with control having no nitrogen application were taken as treatments. There were altogether eight treatments with three replications in a randomized block design.

23 days old brinjal seedlings of the variety Pusa Purple Long were transplanted in plots of 12 sq. metre

with 80 cm. $\times$ 80 cm. planting distances. Phosphorus and potassium at the rate of 15 and 30 kg./ha. respectively were applied in the form of single superphosphate and muriate of potash as basal application. The nitrogen in the form of urea was applied in two split doses, half at the time of land preparation and the remaining half during the first earthing up operation, 25 days after transplanting.

The leaf hopper population for each treatment was recorded early in the morning by selecting 4 plants from each plot randomly, starting from 35 days after transplanting and thereafter at 10 days' interval. The infested fruits having borer holes were separated out from the total harvest per plot in each picking and recorded separately. The uninfested fruits constitute the marketable yield. The moisture and nitrogen percentage were analysed 70 days after transplanting. The nitrogen percentage was analysed with microkjeldahl method.

Results

Data in respect of leaf hopper population, percentage fruit borer infestation, yield and plant analysis were recorded (Tables 1-3).

Average Leaf Hopper Population: It is evident (Table 1) that significant differences at 1 per cent level

exist between the treatments in respect of average leaf hopper population in different ages of the plant. A minimum number of leaf hoppers was observed in No plots followed by N₂₀ and varied significantly from all other treatments. A maximum leaf hopper population was obtained in N₁₂₀, followed by N₁₀₀ and the variation in the population was found to be significant from all other treatments.

TABLE 1—AVERAGE LEAF HOPPER POPULATION PER PLANT IN DIFFERENT STAGES OF PLANT GROWTH

'N' Level	Age of the Plant				
	35 DAT	45 DAT	55 DAT	65 DAT	75 DAT
N ₀	5.80	9.00	12.13	15.63	27.63
N ₂₀	12.86	14.63	22.53	24.90	38.70
N ₄₀	19.80	25.56	39.53	44.86	46.50
N ₆₀	19.90	29.30	45.56	46.53	44.20
N ₈₀	28.13	48.66	49.96	66.56	60.80
N ₁₀₀	48.16	61.03	75.46	120.63	105.06
N ₁₂₀	57.70	77.30	82.23	124.83	109.23
N ₁₄₀	53.40	77.56	76.20	117.86	108.50
'F' Test	**	**	**	**	**
C. D. (P=0.05)	9.97	9.33	7.53	17.95	12.98
C. D. (P=0.01)	13.84	12.95	10.45	24.92	18.01

** Significant at 1 % level.
DAT Days after transplanting.

Fruit Borer Damage : The minimum fruit borer damage (22.83 per cent) was found in No and the maximum (33.08 per cent) was in N₁₂₀. The treatment effect was not found to be significant.

Total Yield: A maximum fruit yield was obtained in N₁₂₀ which was as high as 26.89 te/ha., followed by those in N₁₀₀ (26.34 te/ha.) and N₈₀ (25.33 te/ha.) and varied from all other treatments upto 1 per cent level of significance. The minimum yield (10.04 te/ha.) was obtained in N₀ and varied significantly from all other treatments upto 5 per cent level but no variation was obtained with N₂₀ and N₄₀ upto 1 per cent level of significance (Table 2).

Marketable Yield : The maximum marketable fruit yield was obtained in N₁₄₀ followed by those in N₁₂₀, N₁₀₀ and N₈₀ and it varied significantly from all other treatments upto 1 per cent level. The minimum yield was obtained in N₀ and the variation in respect of yield from all other treatments was observed to be significant upto 5 per cent level but no variation was obtained with N₂₀ and N₄₀ when tested at 1 per cent level of significance.

Moisture : The moisture percentage varied from 80.97 in N₁₄₀ to 81.77 in N₀ (Table 3). The treatment effect was not found to be significant.

TABLE 2—FRUIT BORER INFESTATION AND TOTAL AND MARKETABLE YIELDS UNDER DIFFERENT TREATMENTS:

Level of Nutrient	Fruit Borer Infestation,* %	Total Yield, tons/ha.	Marketable yield, tons/ha.	Fruit Loss due to Borer tons/ha.
N ₀	22.83	10.04	8.50	1.55
N ₂₀	25.32	14.09	11.44	2.65
N ₄₀	29.44	14.31	10.72	3.59
N ₆₀	33.08	19.45	13.79	5.66
N ₈₀	31.00	25.33	18.39	6.94
N ₁₀₀	32.77	26.34	18.51	7.83
N ₁₂₀	33.79	26.89	18.62	8.27
N ₁₄₀	29.34	25.57	19.44	6.13
'F' Test	N.S	**	**	—
C. D. (P=0.05)	—	3.95	2.30	—
(P=0.01)	—	5.48	3.19	—

* Angular transformed value
** Significant upto 1 % level

Nitrogen : The lowest nitrogen percentage was obtained in N₀, followed by those in N₂₀ and N₄₀, the percentage varied significantly from all other treatments. The highest percentage of nitrogen was obtained in N₁₂₀, followed by those in N₁₄₀, N₁₀₀ and N₈₀ (Table 3).

TABLE 3—PLANT ANALYSIS AND AVERAGE NUMBER OF LEAVES PER PLANT IN EACH TREATMENT

Levels of Nutrients	Nitrogen, %	Moisture, %	Average Number of Leaves/Plant
N ₀	3.66	81.77	83.83
N ₂₀	4.04	81.15	78.83
N ₄₀	3.77	81.23	116.66
N ₆₀	4.24	81.38	96.66
N ₈₀	4.26	81.04	91.08
N ₁₀₀	4.58	81.30	102.58
N ₁₂₀	4.80	81.03	116.33
N ₁₄₀	4.59	80.97	102.83
'F' Test	**	N. S.	N. S.
C. D. (P=0.05)	0.54	—	—
C. D. (P=0.01)	0.75	—	—

N. S.=Not significant.

Discussion

The results of the present study indicated that with the increase in nitrogen application there was a corresponding increase in leaf hopper population on brinjal leaves. This increase was obtained in a more or less linear fashion upto N₁₂₀. In N₁₄₀, however, a slight decrease in the leaf hopper population, nitrogen percen-

tage of plant and total yield was obtained, which probably was due to the interaction or interference of other nutrients at this dose which was reflected on the characters studied. The data on the moisture and nitrogen contents and also the number of leaves, which was presumed to be related with more nitrogen application showed the significant relationship only with nitrogen content of the plant (Table 3). This signifies that the nymphs of the leaf hoppers became adult on plants at higher fertility levels and produced significantly more progeny than those on plants without or with 20 Kg/ha. of nitrogen. Several authors^{7,8} have shown that the fecundity of the insect increases with the nitrogen content of the host. In case of fruit borer infestation, although the same trend was obtained as in the case of leaf hoppers, the treatment effect was not found to be significant. This confirms the observation made by the present authors in their earlier work⁵ with the same crop where it was pointed out that the fruit borer infestation was related only with the varietal character of the host plant.

Though quite a sizable amount of unmarketable fruit was obtained in higher nitrogen application which was as high as 8.27 te/ha in N₁₂₀ in comparison to only 1.55 te/ha in No yet there is no sound reason to believe that we should starve the plants into unproductive state in order to escape pest attack. At the same time, one

should take this into account when estimating the economics of fertilizer use. Therefore, higher levels of nitrogen application must be accompanied by adequate pest control measures in order to obtain the highest dividend on productive soils.

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Superphosphate, nitrophosphate and dicalcium phosphate tagged with ^{32}P were tested on wetland paddy at two levels each in pot culture experiment. All the three fertilizers performed equally in respect of dry matter yield, total phosphorus uptake and fertilizer phosphorus uptake. A higher per cent utilization of fertilizer phosphorus was noticed at lower level of fertilizer. Densitometric study of the plant autoradiographs showed maximum accumulation of fertilizer phosphorus in the culm, followed by in leaf sheath and accumulation in leaf blades being the least.

Evaluation of Phosphatic Fertilizers on Wetland Paddy Using ^{32}P as Tracer*

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Phosphatic fertilizers when added to soil undergo a series of chemical reactions^{1,2}, which ultimately affect the availability and uptake of phosphorus^{3,4}. The rate and type of these reactions are largely dependent on soil factors⁵, type of fertilizers and management programme⁷. Much work has been done earlier to elucidate the agronomical value of several phosphatic fertilizers on upland soils⁸. But paddy is cultivated mostly under water-logged soil condition. The submerged condition of soil creates some dynamic changes in the physico-chemical characteristics of soil⁹ which are quite different from the upland soils. These changes in soil characteristics have great influence on the nutrient availability and fertilizer response. In this context, evaluation of phosphatic fertilizers in the specific system of water management, i.e. in submerged condition, becomes essential. Moreover, higher solubility of fixed phosphorus in soil under water-logged condition¹⁰ initiates further interesting question on the performance of less soluble phosphatics. In the present investigation, attempts have, therefore, been made to study the yield, uptake, utilization and distribution of phosphorus in wetland paddy from superphosphate, nitrophosphate and dicalcium phosphate, using ^{32}P as tracer.

Experimental

Soil samples (0-15 cm.), for this pot culture study were collected from the FCI farm at Sindri. The fertilizer materials, i.e. superphosphate, nitrophosphate and dicalcium phosphate, were prepared in the laboratory by acidulation of rock phosphate with sulphuric, nitric and hydrochloric acids respectively^{11,12} and tagged with ^{32}P at the rate of 0.3 mci./gP. The chemical analysis

of soil and fertilizers are given in Table 1. Fertilizers were applied at the rate of 20 and 40 kg. phosphorus/ha respectively and the levels of nitrogen and potassium for all the treatment combinations were adjusted at 100 kg N and 20 kg K per ha. The requisite amounts of fertilizers were mixed with 3 kg. soil, puddled thoroughly and IR-8 paddy seedlings of 25 days age were transplanted. Plants were then allowed to grow under submerged condition for 35 days and the above ground portion were harvested at the tillering stage for dry matter yield, chemical and radio-chemical analysis. After drying and grinding plant samples were digested with triacid mixture (nitric, sulphuric and perchloric acids in the proportion of 10:1:4) and total phosphorus was estimated by chlorostannous reduced molybdophosphoric acid blue colour method in hydrochloric acid system¹³. ^{32}P counting was done using G.M. end window tube connected to the utility scaler. For autoradiographic study, plant samples were harvested after 15 days' transplanting.

Results and Discussion

Results showed that dry matter yield (Table 2), when averaged over levels of fertilizers, were almost similar for all the 3 phosphatic fertilizers. The results regarding total uptake of phosphorus by plants showed similar trend as observed in dry matter yield. The uptake of fertilizer phosphorus was also observed to be similar in all the treatment combinations. Under water-logged condition, soil phosphorus becomes more available¹⁰ (Table 1) and the major proportion of water-soluble phosphorus from the fertilizers are rapidly converted to unavailable form¹⁴. Both these criteria are likely to

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TABLE 1—CHEMICAL ANALYSIS OF SOIL AND FERTILIZERS

Characters	Soil	Fertilizers		
		Dicalcium Phosphate	Super-phosphate	Nitro-phosphate
pH	6.4	2.7	2.5	4.4
C.E.C., me/100 g. soil	10.2	—	—	—
Organic Carbon, %	0.71	—	—	—
Total P, %	0.027	8.2	6.3	7.5
Available P in Dry Soil, ppm	6.3	—	—	—
Available P in Water-logged Soil, ppm	19.3	—	—	—
Water-Soluble P, %	Trace	1.2	86.3	32.1
Total N, %	—	—	—	16.5

TABLE 2—YIELD AND PHOSPHORUS UPTAKE

Characters Studied		Dry Matter Yield, g.	Total P Up-take, mg.	P Up-take from Soil, mg.	P Up-take from Fertilizer, mg	% Utilization of Added Phosphorus
Treatments						
Dicalcium Phosphate	L ₁	5.01	7.2	4.8	2.4	8.0
	L ₂	5.17	7.9	4.1	2.8	4.6
	Mean	5.09	7.5	4.6	2.6	6.3
Nitrophosphate	L ₁	5.17	7.1	4.6	2.5	8.3
	L ₂	5.82	8.1	4.8	3.3	5.5
	Mean	5.49	7.6	4.7	2.9	6.9
Superphosphate	L ₁	5.12	7.0	4.7	2.3	7.6
	L ₂	5.42	8.3	5.2	3.1	5.2
	Mean	5.27	7.6	4.9	2.7	6.4
Control		4.66	5.6	5.6	—	—
CD at 5% level		0.59	1.76	Not significant	Not significant	1.26

L₁ = First level of fertilizerL₂ = Second level of fertilizer

be responsible for equal performance of the fertilizers having different degrees of water-solubility. Similar response to completely or partially water-soluble phosphatics has also been reported by Atanasiu¹⁵. In general, fertilizer application produced significantly higher yield than control suggesting a positive response of phosphorus on paddy. But with the increase in level of fertilizers there was no prominent increase in yield. Data on per cent utilization of added phosphorus revealed lower utilization of fertilizer phosphorus at higher dose which indicated greater importance of soil phosphorus under water-logged paddy. This was further substantiated from the observation that relative proportion of soil phosphorus uptake was more than fertilizer phosphorus uptake. Optical densities measured from the autoradiographs of different plants (Table 3) clearly showed that the concentration of fertilizer

phosphorus was very much higher in the culm followed by leaf sheath and lamina. As maristematic activity is very high at this portion of the culm during this age of plants more concentration of phosphate is likely to occur at this region.

TABLE 3—OPTICAL DENSITIES OF THE. AUTORADIOGRAPHS

Plant Parts		Culm	Leaf Sheath	Leaf Blade	Mean
Treatments					
Dicalcium Phosphate	L ₁	0.36	0.22	0.05	0.21
	L ₂	0.92	0.41	0.23	0.52
	Mean	0.64	0.31	0.14	0.36
Nitrophosphate	L ₁	0.48	0.25	0.13	0.28
	L ₂	0.92	0.47	0.29	0.55
	Mean	0.71	0.36	0.20	0.42
Superphosphate	L ₁	0.32	0.19	0.05	0.18
	L ₂	0.92	0.62	0.25	0.59
	Mean	0.61	0.41	0.15	0.39

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Fourteen soils comprising eight soil associations from Bihar were incubated at room temperature (30-38°C) under submerged conditions. Available iron, available manganese, easily reducible manganese and pH were determined after 7, 30 and 60 days' incubation. The pH of acidic and neutral soils increased during the early period of water-logging followed by a gradual decrease. In calcareous soils the pH decreased gradually. The available iron increased with the increase in period of water-logging. The increase was more pronounced in red and yellow sedentary soils. The available manganese also increased due to water-logging from two to twentyfour fold. Easily reducible manganese decreased at the initial period of submergence followed by an increase.

Iron and Manganese Availability in Paddy Soils of Bihar Under Water-logged Condition

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Introduction

Iron and manganese play a very important role in the nutrition of paddy plants. Gericke¹ found that iron had to be added more frequently to the nutrient solution for young paddy seedlings than to those for wheat, barley, rye and oats grown under the same conditions. He further observed that paddy required available iron in culture solution longer than any other element except nitrogen and potassium. Aiyer² found that paddy required iron and manganese in much larger quantities than other minor elements. A 10 per cent increase in yield was obtained in Japan by the addition of iron and manganese³. Clark *et al*⁴ observed a marked yield response to manganese by paddy plants and concluded that paddy has a high requirement for and exceptionally high tolerance towards manganese.

The occurrence of large amounts of iron and manganese in waterlogged soils has been reported by several workers⁵⁻⁸. In India, Dey and Mandal⁵ found a gradual increase in Fe²⁺ contents of the percolates from two soils kept under submerged conditions. Mandal⁶, while tracing the course of transformation, has also reported an increase in iron and manganese concentration in the Chinsurah (West Bengal) soil. Takkar⁹ and Shrivastava *et al*¹⁰ have studied iron and manganese transformations under waterlogged and subsaturated conditions in four soils of Punjab and three soils of Bihar respectively. Thus, a very few studies have been made on the

availability of iron and manganese in the waterlogged soils.

The present study was undertaken to determine the changes in available iron, available and easily reducible manganese due to waterlogging in representative soil types of Bihar where paddy is very widely cultivated.

Experimental

14 soils (0-15 cm.) from three important groups comprising eight soil associations were collected from the paddy-growing regions of Bihar. The soils had varying physical and chemical characteristics (Table 1). Incubation studies were carried out at room temperature (30-38°C) under submerged conditions. 10 g. of each soil was kept in glass tubes (2.5×15 cm.) under 1 cm. layer of water. The water level was maintained constant by periodic additions of distilled water. 7 sets of fourteen tubes each were kept under incubation; in one set pH measurement was done, in three sets available iron and in the remaining three sets available manganese and easily reducible manganese were determined at intervals of 7, 30 and 60 days. At the end of the specified period complete amount of soil along with water from the tube was removed and used for extraction.

pH measurements were made using a combined electrode with pH meter*. It was measured by just piercing the electrode about 1 cm. deep in the soil, at one hour

*Manufactured by Toshniwal & Bros. Pvt. Ltd. (Cat. No. 41)

(0 days), 7, 30 and 60 days after waterlogging. Air-dry soils were tested for mechanical analysis by the International pipette method, calcium carbonate by rapid titration method and organic carbon by Walkley and Black method¹¹ and cation-exchange capacity by the method described by Jackson¹². The available iron (combined exchangeable Fe^{2+} , Fe^{3+} and dilute acid soluble) was extracted with 1 N ammonium acetate (pH 3.0) and determined colorimetrically by 0-phenanthroline red ferrous complex method after reduction with hydroxylamine hydrochloride¹². The available manganese (water-soluble + exchangeable) was extracted with 1 N neutral ammonium acetate and easily reducible manganese with 1 N neutral ammonium acetate containing 0.2 per cent hydroquinone and determined by periodate method¹². The total iron and manganese were extracted by fusion with sodium carbonate and determined colorimetrically¹².

Results and Discussion

pH: The experimental soils varied widely in their pH from 4.9 to 8.4 (Table 1). The sedentary soils were acidic except Giridih which was neutral (pH 7.1). The soils of alluvial-noncalcareous group were also acidic in reaction except that of Mithapur (pH 7.9), while the alluvial-calcareous soils were alkaline. The changes in pH due to waterlogging are shown in Table 2 and the group averages are plotted in Fig. 1. In the sedentary and alluvial-non-calcareous soils, the pH values gradually increased due to waterlogging followed by a decrease. The pH of sedentary soils increased upto 7 days of waterlogging and then remained fairly steady upto 30 days of waterlogging followed by a declining trend. The pH of alluvial non-calcareous soils increased gradually due to waterlogging upto 30 days after which a declining trend was observed.

TABLE 1—GENERAL CHARACTERISTICS OF EXPERIMENTAL SOILS

Soil No.	Soil Association	Place	pH	C.E.C., m.e./100g.	Organic Carbon, %	CaCO_3 , %	Total Iron (Fe_2O_3), %	Total Manganese ppm.	Texture
1	2	3	4	5	6	7	8	9	10
I: <i>Sedentary Soils</i> (Red & Yellow)									
1.	Light grey catenary soil	Khunti	5.3	12.2	0.65	0.08	9.32	1107	Sandy clay loam
2.	-do-	Kanke	6.1	6.4	0.39	0.09	2.45	586	Loamy Sand
3.	-do-	Hazaribagh	5.9	17.7	0.38	0.08	4.10	478	Clay
4.	-do-	Giridih	7.1	27.2	0.47	0.02	5.79	391	Sandy clay loam
5.	Hill forest soils of steep slopes highly dissected regions	Ramgarh	6.3	9.6	0.40	0.02	2.96	282	Sandy loam
6.	Red yellow ground water laterite soil	Tatanagar	6.2	15.0	0.45	0.02	5.52	565	Sandy loam
7.	Mixed red-yellow black catenary soils of Singhbhum	Putida (yellow)	6.4	19.4	0.61	0.02	5.79	298	Clay loam
II: <i>Alluvial Non-Calcareous Soils</i>									
8.	Recent alluvium non-calcareous	Kishanganj	4.9	6.7	0.46	0.01	3.75	282	Sandy clay loam
9.	Recent alluvium <i>Tarai</i> soils	Araria	5.2	19.3	0.38	0.01	4.25	195	Sandy loam
10.	<i>Tal</i> land soils light grey dark grey medium to heavy textured soils	Danapur	6.5	39.0	0.63	0.01	2.44	387	Clay
11.	<i>Tal</i> land soils light grey dark grey medium to heavy textured soils	Mithapur	7.9	47.4	0.68	0.40	6.74	782	Clay
III: <i>Alluvial Calcareous Soils</i>									
12.	Young alluvium calcareous	Muradpur	8.4	21.3	0.29	3.90	4.89	283	Clay loam
13.	Young alluvium calcareous	Samastipur	7.8	21.4	0.41	21.30	2.52	187	Loam
14.	Young alluvium calcareous	Mushari	7.9	17.7	0.36	24.10	2.32	195	Clay loam

TABLE 2—CHANGES IN pH

Soil No.	Days			
	0	7	30	60
I: <i>Sedentary Soils</i> (Red & Yellow)				
1	5.3	5.6	5.4	4.8
2	6.1	6.4	6.0	5.1
3	5.9	6.2	6.2	5.1
4	7.1	7.6	7.3	6.8
5	6.3	6.8	6.3	5.5
6	6.2	7.2	7.3	7.1
7	6.4	6.8	6.9	6.7
Average	6.2	6.6	6.5	5.9
II: <i>Alluvial Non-Calcareous</i>				
8	4.9	5.7	6.2	4.8
9	5.2	5.7	6.2	4.6
10	6.5	7.0	6.9	7.0
11	7.9	8.1	7.9	7.7
Average	6.1	6.6	6.8	6.0
III: <i>Alluvial Calcareous</i>				
12	8.4	8.2	8.1	7.8
13	7.8	8.0	8.0	7.7
14	7.9	7.9	8.0	7.8
Average	8.0	8.0	8.0	7.8

The increase in pH of acidic soils due to waterlogging may be attributed to the reduction of soil components and resultant formation and accumulation of ammonia, $\text{Fe}_3(\text{OH})_8$, FeCO_3 and $\text{Mn}(\text{OH})_3$ in the system^{9,13,14}. The decrease in pH at 60 days period appeared to be a temporary phase and it may again increase to stabilize near neutrality with the increase in period of waterlogging, as observed by other workers^{13,15}. However, further studies are needed to explain such dynamic changes in the pH of submaerged soils.

The alluvial calcareous soils showed very little changes and the average pH remained constant upto a period of 30 days and decreased thereafter (Table 2 and Fig. 1). Similar results were obtained by Ponnampereuma *et al*¹⁵, who defined the decrease in pH of the calcareous soils by the partial pressure of carbon dioxide through $\text{CaCO}_3 - \text{H}_2\text{O} - \text{CO}_2$ system.

Iron : Red-yellow light grey catenary soil of Khunti having acidic pH contained maximum total iron of 9.32 per cent, while young alluvium calcareous soil of Mushari had 2.32 per cent iron, minimum among all the 14 experimental soils (Table 1). The total iron content of sedentary soils was more compared to alluvial soils (both calcareous and non-calcareous), which may be due to the presence of iron-rich minerals in their parent material¹⁶.

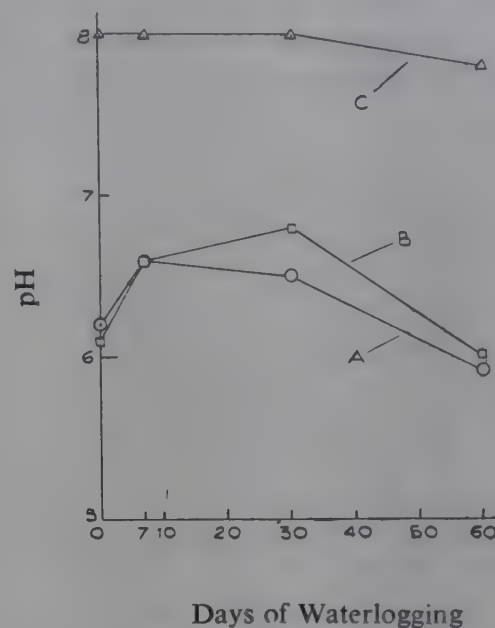


Fig 1. Changes in pH

A—Sedentary Soils
B—Alluvial Non-calcareous Soils
C—Alluvial Calcareous Soils

The available iron in air-dry samples varied from 25 (Muradpur and Khunti) to 380 ppm (Mushari) (Table 3). The amount of available iron present in the soils followed the order : alluvial calcareous > alluvial non-calcareous > sedentary soils. Dubey *et al*¹⁷ have also reported higher available iron in alluvial soils than the sedentary soils which contain much higher amount of total iron. The available iron increased with the period of waterlogging in all the soils (Table 3). The degree of increase was more in acidic soils than in neutral and alkaline soils. Fig. 2 indicate that the order of increase in the amount of available iron was as follows : sedentary soils > alluvial non-calcareous soils > alluvial calcareous soils. These observations are in agreement with the findings of Takkar⁹. A maximum increase in available iron after 90 days was observed in Khunti soil, having pH 5.3, organic carbon 0.65 and Fe_2O_3 9.32 per cent. A minimum increase was observed in Muradpur soil having pH 8.4, organic carbon 0.29 per cent and Fe_2O_3 4.89 per cent. Thus, it can be seen that (i) lower initial pH, (ii) high total iron content, and

(iii) high organic carbon favour greater increase in availability of iron under waterlogged condition¹³.

The increase in available iron in all the soils after water-logging can be attributed to the reduction of iron from insoluble Fe^{3+} to more soluble Fe^{2+} . The reduction takes place due to anaerobic metabolism of bacteria and appears to be chiefly a chemical reduction of Fe^{3+} by bacterial metabolites¹³. Kumura, Takai and Ishikawa¹⁸ pointed out that along with bacterial reduction respiration may also be involved. These findings are in agreement with those of Islam and Elahi¹⁹, Mandal⁶, Motomura²⁰, Kumada and Asami²¹ and Takkar⁹.

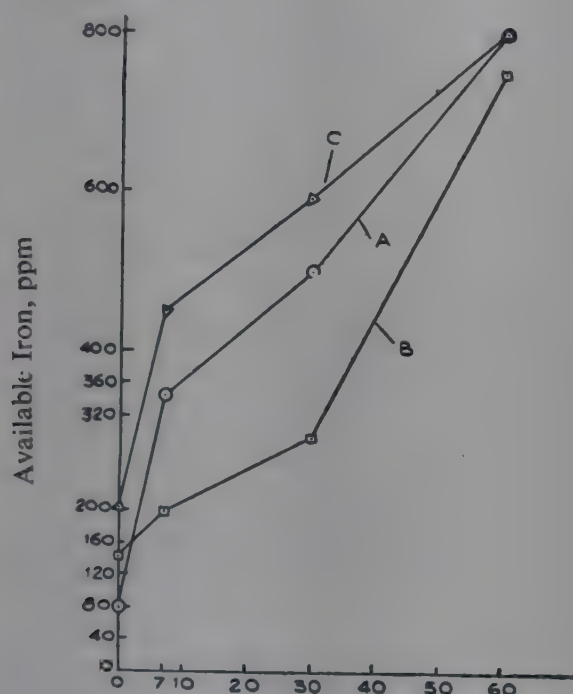


Fig 2. Changes in Iron

A—Sedentary Soils
B—Alluvial Non-calcareous Soils
C—Alluvial Calcareous Soils

Manganese: The red-yellow—light-grey catenary soil of Khunti having acidic pH contained maximum amount of total manganese (1107 ppm), while minimum amount of total manganese was present in young aluvium calcareous soil of Samastipur (187 ppm) having alkaline pH. The available manganese content varied from 5 (Mithapur and Muradpur) to 92 ppm (Khunti). In general, acidic soils had higher available manganese compared to alkaline soils. (Table 3). Easily reducible manganese varied from 13 ppm. in Mushari soil to 280 ppm in Giridih soil (Table 3). All the three types of manganese viz., total, available and easily reducible were higher in sedentary soils than alluvial non-calcareous

and alluvial calcareous soils (Table 1). This is in agreement with the observations of Dubey *et al*¹⁷.

In all the soils, available manganese increased with the period of waterlogging but in five soils it decreased slightly at 30 days, followed by an increase at 60 days period (Table 3). Soils of all the three groups exhibited similar pattern of changes in the concentration of available manganese with the period of waterlogging. Increase was more pronounced at 7 and 60 days period. In between 7 and 30 days period a slow increase in sedentary and alluvial non-calcareous soils and a slight decrease in alluvial calcareous soils was observed (Fig. 3). The groupwise order of increase in available manganese due to waterlogging was: Alluvial-non-calcareous soils > alluvial non-calcareous soils > sedentary soils (Fig. 3). The increase in the availability of manganese is due to reduction of higher oxides of manganese (dioxide, trioxide and tetraoxide), which may result from these compounds functioning as (i) electron acceptors in the respiration of micro-organisms and (ii) chemical oxidants of reduction products¹³.

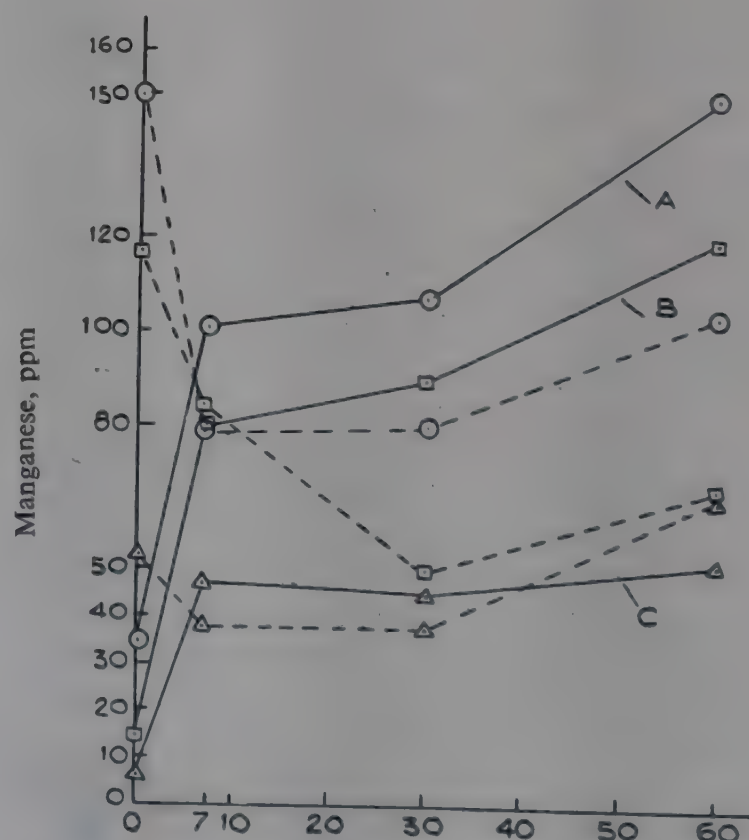


Fig 3. Changes in Manganese

A—Sedentary Soils
B—Alluvial Non-Calcareous Soils
C—Alluvial Calcareous Soils

dotted lines—Easily Reducible Manganese
full lines—Available Manganese

Easily reducible manganese decreased in the early stages of waterlogging in 12 soils but in Danapur soil it remained the same, while it increased in Mushari soil (Table 3). At 30 days period easily reducible manganese decreased in 7 soils remained constant in one and increased in remaining six soils. But at 60 days period this form of manganese increased in all the soils. This may be attributed to partial transformation of total insoluble Mn to easily reducible Mn, after certain period of waterlogging when intense reducing conditions sets in. These observations agree with the findings of Mandal⁶

Increase in the available Mn and decrease in the easily reducible manganese in almost all soils irrespec-

tive of their general characteristics at initial stages of waterlogging was noted (Table 3). It can be seen from the nature of the curves in Fig. 3, that both the forms of manganese are in equilibrium with each other. This supports the existence of manganese cycle in soil in which all the forms of manganese are believed to be in dynamic equilibrium with each other²²⁻²⁴.

Acknowledgements

Thanks are due to Dr. D. L. Deb, formerly Technologist, in P and D Division, FCI Ltd. and now working in I.A.R.I., New Delhi, for initiating the work and to Dr. S. N. Basu, Senior Soil Chemist, for his assistance in preparing the manuscript.

TABLE 3—CHANGES IN AVAILABLE IRON, AVAILABLE MANGANESE AND EASILY REDUCIBLE MANGANESE

Soil No.	Available Iron, ppm				Available Manganese, ppm				Easily Reducible Manganese, ppm			
	0	7	30	60	0	7	30	60	0	7	30	60
I: <i>Sedentary Soils (Red & Yellow)</i>												
1.	25	167	483	1482	92	127	174	178	224	202	184	193
2.	80	475	552	765	50	80	118	298	107	48	92	97
3.	65	390	476	831	21	93	114	117	112	45	21	40
4.	110	212	386	507	6	142	98	143	280	115	123	157
5.	65	212	484	615	22	99	114	143	131	50	54	84
6.	60	649	778	808	36	39	56	69	39	22	22	40
7.	155	300	345	598	14	128	78	98	163	71	61	119
Average	80	343	500	801	34	101	107	149	151	79	80	104
II: <i>Alluvial non-Calcareous</i>												
8.	135	176	279	583	15	57	79	115	39	23	27	54
9.	120	150	205	986	6	60	70	83	23	17	20	50
10.	125	193	303	904	31	121	167	184	193	193	103	58
11.	200	280	384	521	5	83	43	97	214	103	50	112
Average	145	200	293	748	14	80	90	120	117	84	50	68
III: <i>Alluvial Calcareous</i>												
12.	25	34	49	41	5	67	75	86	120	68	65	125
13.	205	467	765	986	6	39	37	43	22	21	18	35
14.	380	854	959	1370	7	35	23	26	13	25	31	39
Average	203	452	591	799	6	47	45	52	52	38	38	66

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When crystals of $\text{Cu K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is diluted with the corresponding Zn^{2+} Tutton salt, the elongated octahedron, at room temperature, is changed to a compressed one, the symmetry prevailing being orthorhombic. ESR method, as outlined by Bose *et al.*², has been used to determine the orthorhombic orientations in the crystal.

Orthorhombic Orientation of Cu^{2+} Ion in $\text{K}_2(\text{SO}_4)_2$ Lattice Diluted with $\text{Zn K}_2(\text{SO}_4)_2$ at Room Temperature

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The changes in the magnetic axes with dilution in crystals containing less than 1 per cent Cu^{2+} ion in $\text{K}_2(\text{SO}_4)_2$ lattice diluted with corresponding Zn^{2+} salt have been observed by Bagguley and Griffiths¹. For such high dilution, as observed, the elongated octahedron is changed into a compressed one at room temperature. As an approximation, the crystal field was assumed by the above authors as tetragonal. E.s.r. studies^{2,3} of undiluted salts of Cu^{2+} have, however, shown the crystalline field to be definitely orthorhombic, particularly at room temperature. The optical absorption studies of diluted and undiluted salts of Cu^{2+} by the authors (unpublished) and also by Suri and Mathur⁴ have established the orthorhombicity of the field as well as a change in the energy level pattern with very high dilution. Mookherji and Lal⁵, Banerji and Mookherji⁶ explained the results of magnetic susceptibility and anisotropy by assuming a tetragonal field, which, is only approximate. Hence it was considered necessary to undertake e.s.r. studies of the Cu^{2+} ion at such dilutions and to determine the orientation of the unit cell with respect to the magnetic axes, in order to explain in finer details its magnetic behaviour. The method adopted for such determination was that given by Bose *et al.*².

Experimental

Single crystals were grown by aqueous evaporation of the mixed potassium salts and the copper percentage in the crystal was determined by atomic absorption

spectrometer. The crystal in which the measurements were made, contained 0.8762 per cent of copper.

E.s.r. spectra were taken at room temperature in Bruker-Physik B-ER402 spectrometer operating at X-band. Special arrangements for rotating the crystal in the desired plane was made. The measurement was confined to the (001), $[(0\bar{1}1) \text{ or } (011)]$, $[(1\bar{1}0) \text{ or } (110)]$ and $[010]$ planes. Figs. 1, 2 and 3 show a plot of the g^2 against θ values. No clear resolved peaks of the absorption lines for the two ions in the unit cell was obtained in (001) plane as such g^2 vs θ curve for this plane could not be plotted.

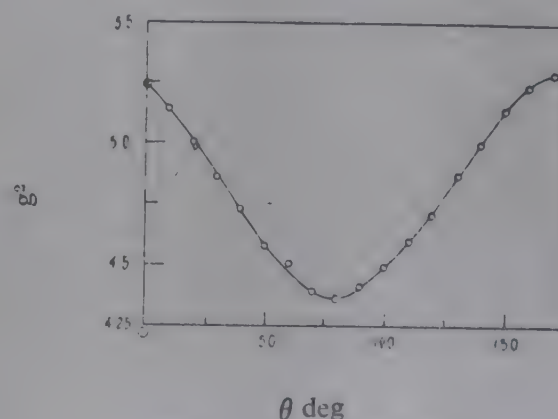


Fig. 1—b-Axis Vertical

Results

The symmetric matrix constructed for the coefficients of the general equation of the ellipsoid with orthogonal axes X, Y, Z where X and Y are the crys-

tallographic a and b axes and Z is perpendicular to ab-plane lying within the obtuse β , is given by

5.105	0.02217	-0.3637
0.02217	4.991	0.3835
-0.3637	0.3835	4.505

The measurement in the (001) plane is done to remove the ambiguity in the value corresponding to the matrix element (12) obtained from measurements in other planes. In the present case, the ambiguous values are 0.2422 and 0.02217. If the former value is assumed then a minimum separation in the g^2 values for the two ions should be greater than 0.1, which could have been easily detectable. Hence, the latter value is taken for the corresponding matrix element.

The principal g^2 values and direction cosines obtained after diagonalizing the above matrix by the method of successive approximation are given below:

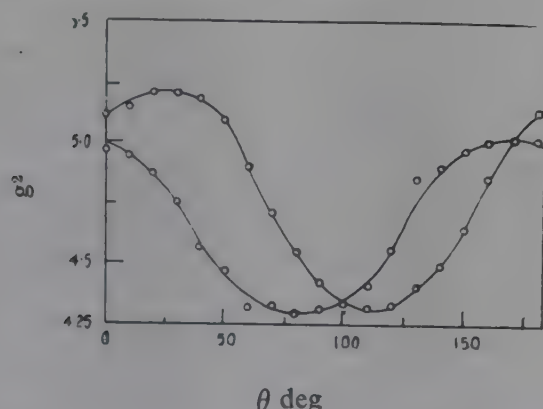


Fig. 2—p-plane ie. $(1\bar{1}0)$ or (110) Horizontal

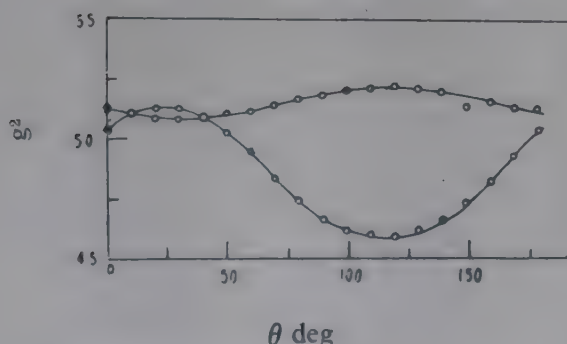


Fig 3—b-plane ie. $(0\bar{1}1)$ or $(0\bar{1}\bar{1})$ Horizontal

$$\begin{matrix} G_1^2 = 5.358 \\ G_2^2 = 4.142 \\ G_3^2 = 5.065 \end{matrix} \begin{bmatrix} 0.6968 & -0.4908 & -0.5222 \\ -0.3463 & 0.4007 & -0.8484 \\ 0.6262 & 0.7714 & 0.1106 \end{bmatrix}$$

This gives the orientations of g-axes with respect to magnetic axes as:

$$\begin{matrix} G_1 = 2.31 \\ G_2 = 2.04 \\ G_3 = 2.26 \end{matrix} \begin{matrix} X_1 & X_2 & X_3 \\ \begin{bmatrix} 143^\circ 53' & 119^\circ 24' & 108^\circ 56' \\ 83^\circ 24' & 66^\circ 22' & 155^\circ 24' \\ 125^\circ 12' & 39^\circ 31' & 74^\circ 24' \end{bmatrix} \end{matrix}$$

Discussion

It is clear from above that the symmetry of the g^2 -ellipsoid for highly diluted salts at 300°K is definitely orthorhombic. A comparison with the undiluted salts demonstrates $g_1 > g_{11}$ for such diluted crystals, if the symmetry is assumed to be tetragonal approximately. Further, G_2 is seen to be the approximate symmetry axis, X_1 being perpendicular to the tetragonal axes and X_2 a bisector. This angle is found to be $24^\circ 36'$. Thus, the elongated octahedron is changed to a compressed one with dilution, the crystalline field symmetry prevailing being orthorhombic.

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Differential scanning calorimetric and gas evolution study of three different binary systems of urea with orthoboric acid, monoammonium phosphate and potassium metaphosphate have been carried out in the range 50-220°C. It has been observed that urea forms an addition compound with boric acid at 70°C with elimination of water. The heat of reaction has been found to be -9.53 K.cal/mole . Monoammonium phosphate undergoes polymerization in presence of urea and its degree decreases with increase of phosphate content. It occurs in two successive stages in the range 110-122°C. These two stages have been characterized by ascertaining their temperature ranges, viz. 110-115 and 115 to 122°C respectively. When KPO_3 is taken there is no such polymerization and instead an eutectic mixture of urea and KPO_3 at 129°C has been formed. The possibility of granulation using this mixture avoiding decomposition of urea has been postulated.

Differential Scanning Calorimetric Study of Some Binary Fertilizer Systems Containing Urea

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Urea, an important fertilizer, is generally used in the soil either as such or after admixture with various other nitrogenous and phosphatic fertilizers and micro-nutrients, like ammonium sulphate, ammonium phosphate, magnesium phosphate, some potassium salts and boron bearing compounds^{1,2}. Generally trace elements like boron, are used as a mechanical mixture with urea³ and the phosphatic fertilizers are used either as a mechanical mixture or in the form of some chemically reacted compound^{1,2}.

Among these boron forms, as reported by Skvortsov *et al*^{4,6}, an addition compound with urea. Ammonium phosphate is known to form condensed ion phosphate, which has recently been reported by Norehaeva *et al*⁷, but physico-chemical properties of such binary systems have not been studied in detail. When ammonium phosphate is replaced by potassium metaphosphate, the urea-phosphate system is expected to be a better fertilizer as it contains all the three essential plant nutrients, viz. nitrogen, phosphorus and potassium. However, its thermal stability has not been studied so far. As such, it would be interesting to know their detailed physico-chemical characteristics, like thermal stability, nature of compound formation, probable composition and energies of such reactions.

In order to throw some light on the above properties, precise thermal studies have been undertaken.

Experimental

Samples used for this investigation were prepared from A.R. quality ingredients which were preserved before use in a desiccator using fused calcium chloride as the dehydrating agent. Binary mixtures containing 100, 75, 67 and 50 molar per cent of urea and orthoboric acid, monoammonium phosphate, potassium metaphosphate were prepared mechanically by using an agate mortar in an air-conditioned room (humidity 60 per cent, temperature 25°C). Such fresh mixtures were immediately subjected to thermal study.

The differential calorimetric study of all these samples and the individual pure components were performed in a differential scanning calorimeter (Perkin-Elmer DSC-1B) in the range 50-180°C. The heating rate was 8°C/min. The samples were taken in standard aluminium pans sealed by a crimping device, so as to withstand a pressure of 30 psi. During the experiment a dynamic nitrogen atmosphere was maintained in the reaction chamber. A sample quantity, 2-5 mg., was sufficient which was used in the powdered form. A similar empty aluminium pan was used as the reference material.

* Paper Presented at the 61st Session of the Indian Science Congress held at Nagpur during January 3-9, 1974.

The energies associated with the reactions were calculated from the areas of the thermograms as measured with the help of a planimeter. Metallic tin was used as an external standard because it has a well-known transition energy (latent heat of fusion = -14.5 cal./g.) in the experimental temperature range and is available in high purity.

The following equation was used for energy calculation :

$$H_{(m)} = \frac{H_{(T)} \times S_{(m)} \times W_{(T)}}{S_{(T)} \times W_{(m)}},$$

where $H_{(T)}$ = heat of fusion of tin, $S_{(m)}$ = area of the transition peak of the mixture, $S_{(T)}$ = area of the transition peak of tin, $W_{(T)}$ = weight of tin, and $W_{(m)}$ = weight of the mixture.

The gas evolution analysis of the mixtures was carried out with the same instrument. In these cases open sample pans were used and the carrier gas was dry nitrogen.

The thermograms are shown in the Figs. 1, 2 and 3. Fig. 4 shows the curves of gas evolution analysis and Fig. 5 the plot of mole fraction of urea in the mixture against temperature. Table 1 shows the observed energies in cal./g. of the sample.

Results and Discussion

In Fig. 1, the curves A and B represent the thermograms of pure urea and orthoboric acid respectively. The single endothermic peak at 136°C in the curve A is due to the melting of urea, and in the curves B the three successive endothermic peaks at 114 , 136 and 169°C are due to the transformation of orthoboric acid to metaboric, pyroboric acid finally B_2O_3 , respectively. All such transformations are reported in the literature^{8,9}. Recent DTA studies of Marano *et al*¹⁰ have indicated peaks for all such transformations. Unlike that of the pure component, a new endothermic peak at 70°C (Fig. 1) appears in all the mechanical mixtures of urea and boric acid and the intensity of the peak corresponding to 2: 1 molar composition is maximum. But in mixtures where urea is higher than this optimum composition a second endothermic peak around 126 to 124°C (Fig. 1, curves C and D) appears and in mixtures having boric acid higher than this composition this peak appears at 140°C . It is interesting that this second peak is totally absent in the thermogram of a mixture having this optimum composition, i.e. urea : boric acid (2: 1). Moreover, the energy of the peak at 70°C of the mixture of 2: 1 molar composition is the highest and is equal to -53 cal/g. This energy decreases uniformly when the urea content increases or decreases beyond this stoichiometric composition (Table 1). Earlier work-

ers reported this compound formation at 60°C . But the present results show formation of this compound at 70°C . Moreover, the gas evolution analysis (Fig. 4 curve E') shows that the compound formation at 70° takes place through elimination of water. It may be pointed out, however, that the second peak, which

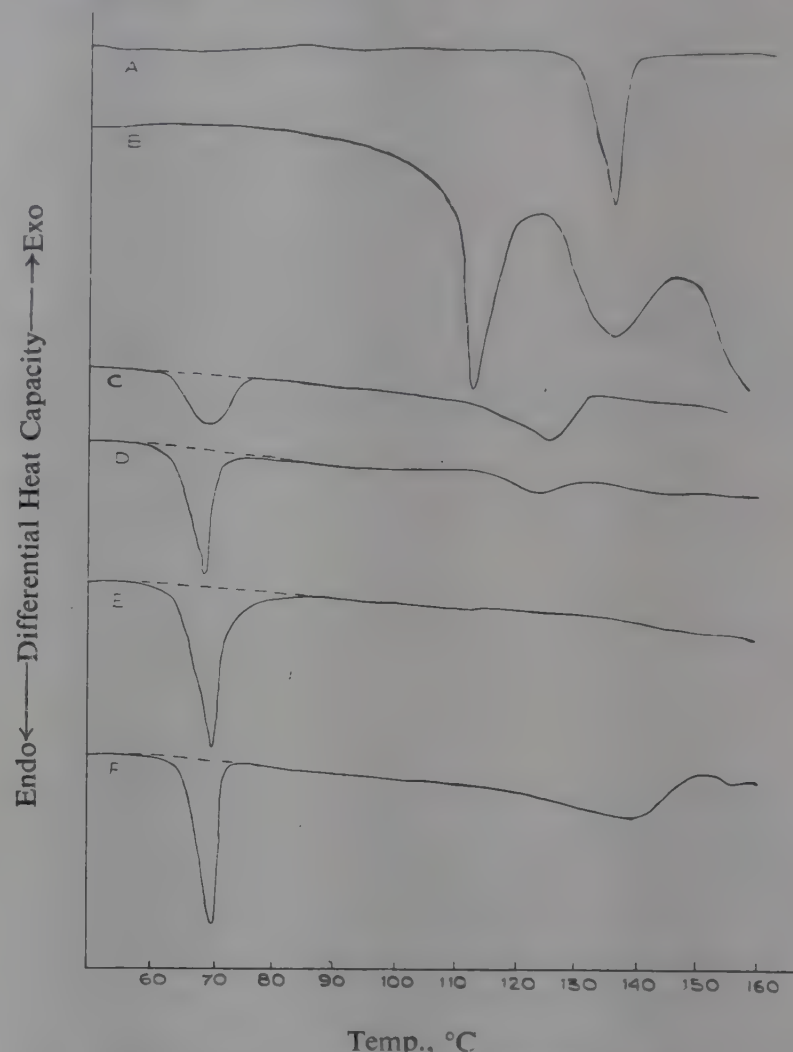


Fig. 1—Thermograms of Pure Urea, Orthoboric Acid and their Binary mixture [A, B, C, D, E and F represent samples containing 100, 0, 90, 75, 67 and 50 mole % of urea will rest of orthoboric acid]

appears either at 124 - 126°C , or 140°C , is due to melting of free urea and final transformation of boric acid respectively. This lowering of their melting points may possibly be due to formation of a new compound as a result of solid-solid interaction along with the elimination of water. The details, of the calorimetric study on this system have been published¹¹.

In the Fig. 2, curve G represents the thermogram of pure monoammonium phosphate having a single endothermic effect at 205°C , which is definitely due to its melting as reported by Nabier *et al*¹². Urea is known to give an endothermic effect at 136°C (Fig. 1, curve A). But their molar mixtures give an altogether new double-natured endothermic peak in the range 110 - 122°C (Fig. 2, curves K, J, I and H) and throughout the rest of the thermogram no other peak is present. These

double-natured peaks may be considered as the combination of two different endothermic effects having very close energy changes. The first set of peaks appears in the range 110-115°C (Fig. 2, curves K to H) and the second set appears in the range 115-122°C.

TABLE 1—OBSERVED ENERGIES FROM DIFFERENTIAL CALORIMETRIC CURVES

Sample Designation	Composition, Mole %	Energy, cal./g. of sample
Urea:Orthoboric acid		at 70°C
A	100 : 0	—
B	0 : 100	—
C	90 : 10	—15.5
D	75 : 25	—38.4
E	67 : 33	—53.0
F	50 : 50	—39.0
Urea: Monoammonium phosphate		at 110—122°C
G	0 : 100	—
H	90 : 10	—38.0
I	75 : 25	—31.7
J	67 : 33	—27.5
K	50 : 50	—21.4
UREA:KPO ₃		at 129—131°C
L	0 : 100	—
M	90 : 10	—48.7
N	75 : 25	—25.0
O	67 : 33	—20.3
P	50 : 50	—16.1

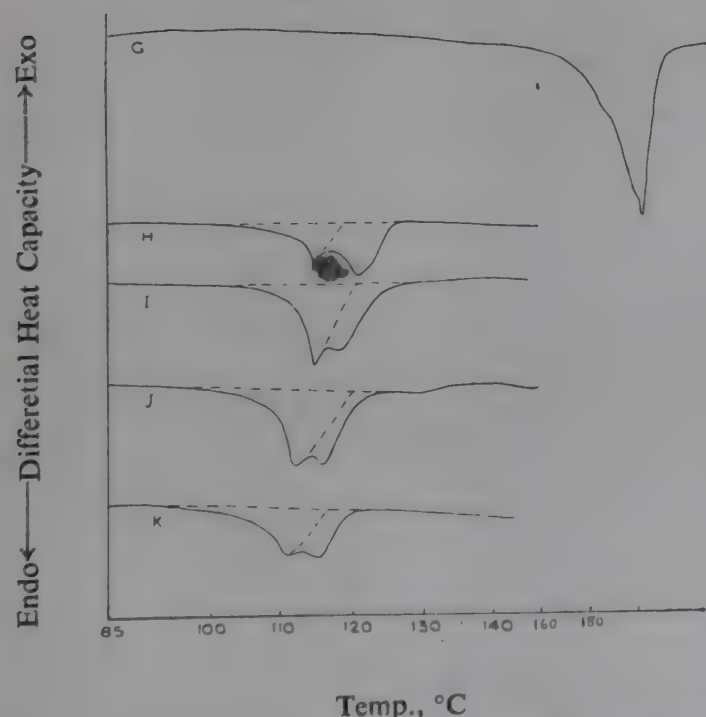


Fig. 2—Thermograms of Pure MAP & Its Binary Mixture with Urea [G, H, I, J & K represent samples containing 0.90, 75, 67 & 50 mole % of urea with rest of ammonium phosphate]

Norchaeva *et al*⁷ has reported the formation of a condensed ion phosphate with urea at 110 to 120°C, where urea acts as a dehydrating agent and accepts the water released during the reaction.

Consequently, the first endothermic effect at 110-115°C may be assigned to be due to the formation of the condensed ion phosphate whereas the second endothermic effect ranging from 115 to 122°C may be due to the final transformation of urea to carbamate in presence of water as indicated by Norchaeva *et al*⁷.

It is interesting to mention here that the energy of formation increases from —21.4 to —38 cal./g. with increase of urea content from 50 to 90. mol. per cent. It is difficult to ascertain the energy of the polymerization and condensation separately from the double nature peak. The observed energy evaluated from their peak (Fig. 2) is thus a sum of these two simultaneous reactions. In spite of the above facts, it may be inferred from this result that energy of polymerization and/or condensation reaction decreases with increase of phosphate content. The former one is possible only when the degree of polymerization decreases. Once this is less, the quantity of water liberated will also be less and the energy of condensation will therefore decrease.

The effluent gas analysis (Fig. 4, curve J') of the 2: 1 molar mixture at the reaction temperature shows no indication of evolution of any gaseous products which strongly supports Norchaeva's views that the water formed during the reaction is taken up by the urea in the mixture.

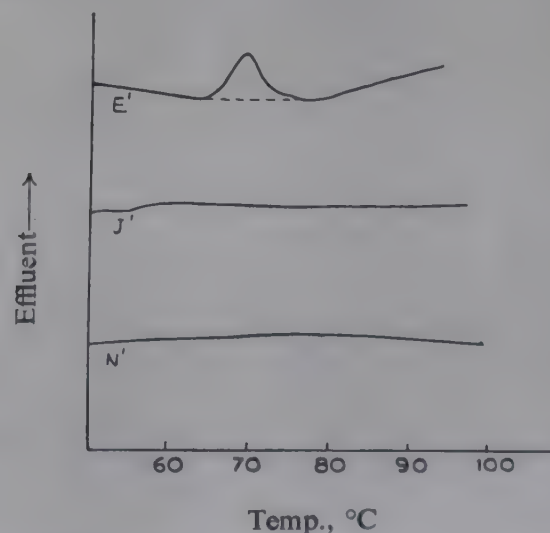


Fig. 4—Effluent Analysis Curves for Binary Mixtures of Urea with Orthoboric Acid, MAP & Potassium Metaphosphate [E' contains 67: 33 mole % of urea ; orthoboric acid ; J'—67: 33 mole % of urea : MAP. N'—67.33 mole % of urea : potassium metaphosphate]

In Fig. 3, the thermogram of pure KPO₃ (curve L) is featureless indicating its inertness in the experimental temperature range. Urea has a well-defined peak at 136°C

due to its melting in its thermogram. This temperature shifts to a lower side when KPO_3 is added. The lowering goes upto 120°C with increase of KPO_3 upto 25 mol.

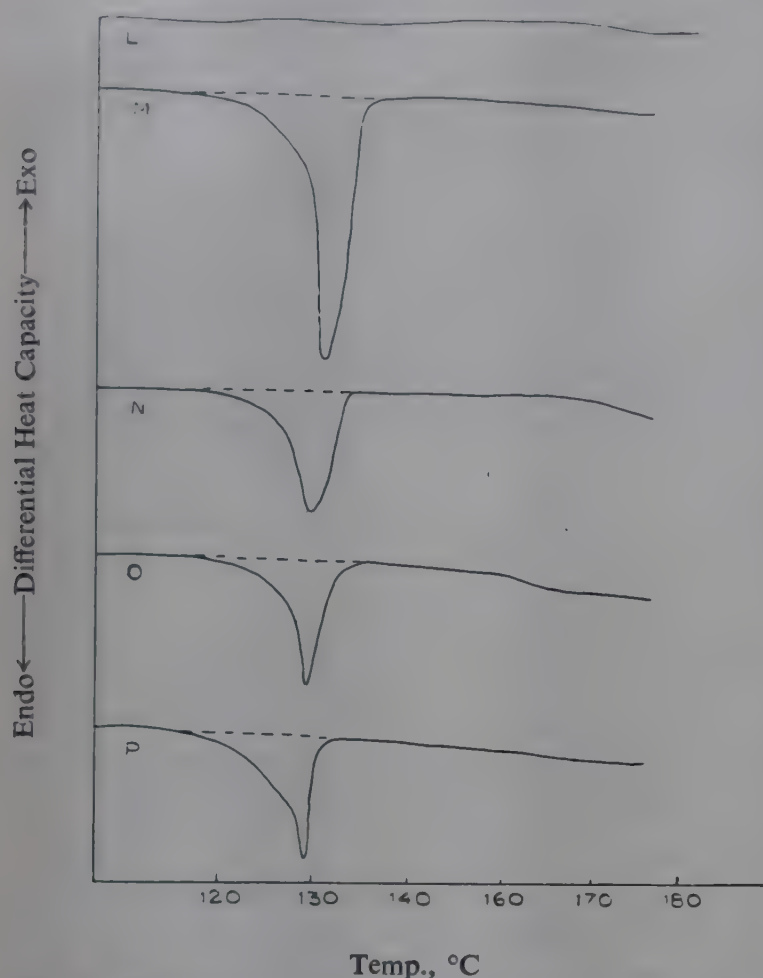


Fig. 3—Thermograms of Pure Potassium Metaphosphate & its Binary Mixtures with Urea [L, M, N, O & P represent samples containing 0, 90, 75, 67 and 50 mole % of urea with rest of potassium metaphosphate]

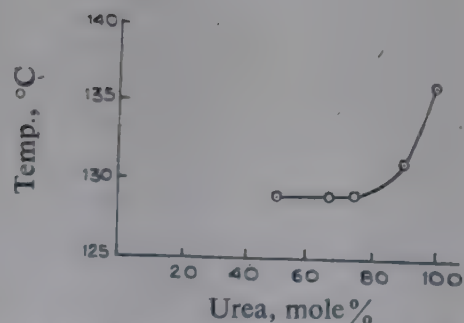


Fig. 5—Plot of Mole Fraction of Urea with Rest of Potassium Metaphosphate Against Temperature

per cent (Fig. 5). It remains constant on further increase upto 50 mol. per cent. Further study has not been made beyond this composition as it exceeds the limit of the practicable formulation of compound fertilizers. The heat of fusion of this mixture at the eutectic composition and temperature is -20.3 cal./g , which increases with urea content in the mixture.

It is, thus, evident that when ammonium phosphate is replaced by potassium metaphosphate there is no polymerization of phosphate in the mixture. Instead an eutectic mixture having melting point 129°C has been found out, which may be useful for granulation purpose as decomposition of urea can be avoided at that temperature.

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Non-destructive neutron activation and x-ray fluorescence techniques have been applied to the analysis of plant nutrients in soil. The advantages of these methods over the conventional ones have also been focussed.

Non-Destructive Plant-Nutrient Analysis by Neutron Activation and X-Ray Fluorescence Techniques

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Plants need a wide variety of elements¹, known as macro-or micro-nutrients, for their sustenance and growth. The macronutrients, constituting the cellular ingredients of the plant, include nitrogen, phosphorus, potassium, magnesium, calcium and sulphur, while those having various metabolic functions consist of iron, manganese, cobalt, zinc, copper, boron, chlorine and molybdenum. In addition, trace amounts of elements, like sodium, aluminium, vanadium and silicon, etc. are also needed for better crop yields. The ensurance for the best crop yield calls for ascertaining the presence and quantitative estimation of these elements in soil so as to optimize its condition by making up the deficiency. The chemical methods employed for the purpose are very lengthy and tedious² besides being insensitive when some of the elements are present in ppm order³.

To circumvent the above limitations, the present authors have employed neutron activation analysis (NAA), which by virtue of its speed, selectivity and sensitivity has dwarfed all physico-chemical methods of analysis reported so far. This technique⁴, in its simplest form, is based on the transmutation of the stable target atom into a radionuclide as a result of irradiation with thermal neutrons. The radionuclide has a definite half-life and shakes off its extra energy by emitting γ -rays. Like half-life, the energies of these γ -rays are characteristic of the radionuclide producing them and, therefore an energy analysis of γ -rays emanating from an unknown sample provides unmistakable 'finger print' of its original elemental composition prior to irradiation. Once an element is posi-

tively identified, its quantitative determination follows from the comparison of its characteristic γ -ray activities in known weights of the sample and a compound of the sought element (standard) both having been subjected to identical conditions of irradiation and counting.

To investigate the exceptional elements, like iron, which have very low thermal neutron cross-section, another device, viz. x-ray fluorescence (XRF) technique⁵, using the excitation of characteristic x-rays of elements by irradiating the unknown sample with monoenergetic γ -sources and measuring the energies and intensities of these x-rays for quantitative estimation of elements, has been adopted.

Experimental

Two soil samples of different origin were crushed, oven-dried, and sieved to obtain particles in 100 mesh (BSS) size. For irradiation, 1.6 g. of the above was loaded into a cylindrical perspex capsule with conical ends and inner cavity measuring 2.54 cm. $\times$ 1 cm. A threaded cap was provided at one end of the capsule for sample transfer. Perspex was chosen as the rabbit material to minimize contribution to activity from the container itself.

The samples were irradiated in the Canada-India reactor (CIRUS) at Bhabha Atomic Research Centre (BARC), Trombay, with a thermal neutron flux of 1.4×10^9 n cm.⁻² sec.⁻¹. Fig. 1 represents the sample-irradiation and counting lay-out. A pneumatic system with aluminium tubings, microswitches and PVC

[illegible]

1. Reactor Wall	7. Gap
2. Thermal column	8. Shielding (Lead, paraffin and Concrete)
3. & 10. Microswitches	9. Shielding (Lead, Steel and wood)
4. Stop-ring for rabbit	11. Rabbit
5. Aluminium tubing	12. NaI (Tl) detector
6. Paraffin plug	

Results and Discussion

times are presented in subsequent figures for half-life ($T_{1/2}$) determinations. The plots for peaks at 0.17 and 1.05 MeV are well defined straight lines (Fig. 3) with slopes corresponding to the $T_{1/2}$ of Mg^{27} (9 min.). Similar plot (Fig. 6) for 2.27 MeV-peak characterizes Mn^{56} ($T_{1/2}$: 2.37 hr.). On the other hand, the plots for 0.87 and 1.8-MeV peaks show curvature pointing to the presence of more than one element. On further analysis, they turn out to be a combination of two straight lines each with slopes corresponding to $T_{1/2}$ of Mn^{56} (2.5 hr.) — Mg^{27} (9 min.) (Fig. 4) and of Mn^{56} (2.58 hr.) — Al^{28} (2.5 min.) (Fig. 5).

Table 1 summarizes the standard and experimentally observed half-life and energy values for the elements found.

Sample No.	Isotope	Half-life			Energy, MeV		
		Standard	Observed	Per- cent Vari- ation	Stan- dard	Obs- erved	Per- cent Vari- ation
1	Mg ²⁷	9.5 min.	9.0 min.	5.3	0.168	0.17	1.2
					0.842	0.87	3.3
					1.010	1.05	4.0
	Mn ⁵⁶	2.58 hr.	2.50 hr.	3.1	0.845	0.87	3.0
			2.58 hr.	0.0	1.81	1.89	4.4
			2.37 hr.	8.1	2.12	2.27	7.1
2	Al ²⁸	2.5 min.	2.5 min.	0.0	1.78	1.8	1.1
	Mn ⁵⁶	2.58 hr.	2.5 hr.	3.7	0.845	0.85	0.6
			2.6 hr.	0.8	1.81	1.89	4.4
			2.4 hr.	7.0	2.12	2.22	4.6
	Na ²⁴	15.0 hr.	15.2 hr.	1.3	1.368	1.42	1.6
					2.75	*	

TECHNOLOGY

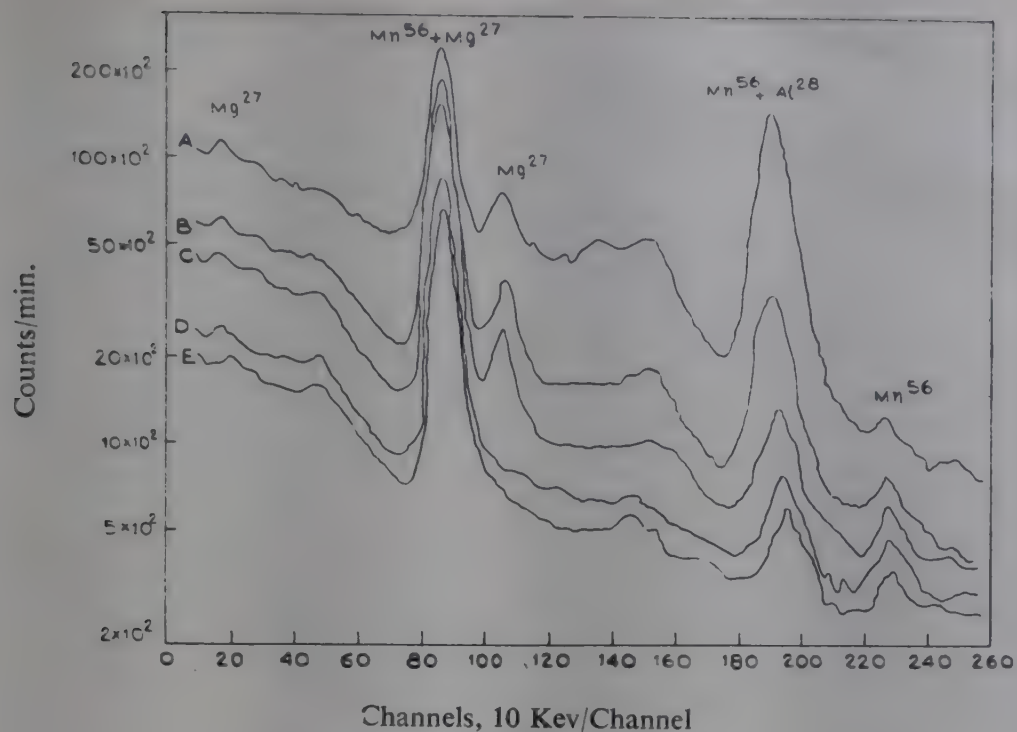


Fig. 2—Decay Spectra of Sample 1

Timings, min.

A = 0 D = 76
B = 6 E = 137
C = 12

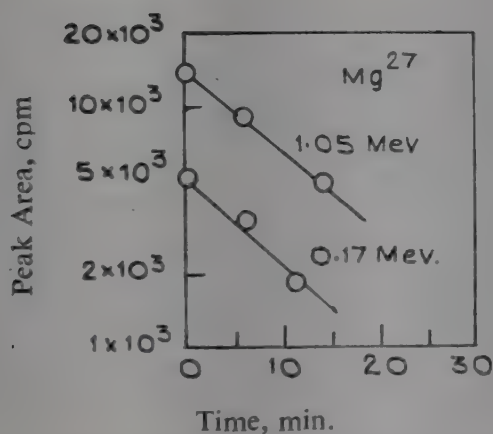


Fig. 3—Half-life Determination of Mg^{27} (Sample 1)
[Observed $T_{1/2}$: 9 min.]

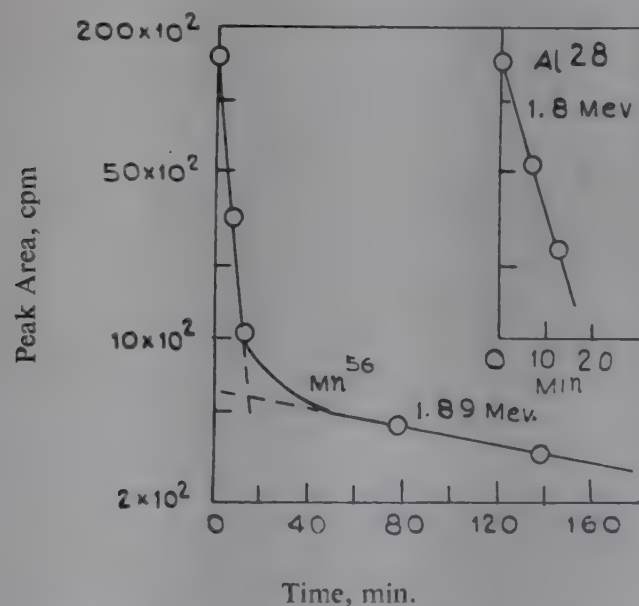


Fig. 5—Half-life Determination of Mn^{56} and Al^{28} (Sample 1)
[Observed $T_{1/2}$: Mn^{56} 2.58 hr; Al^{28} 2.50 min.]

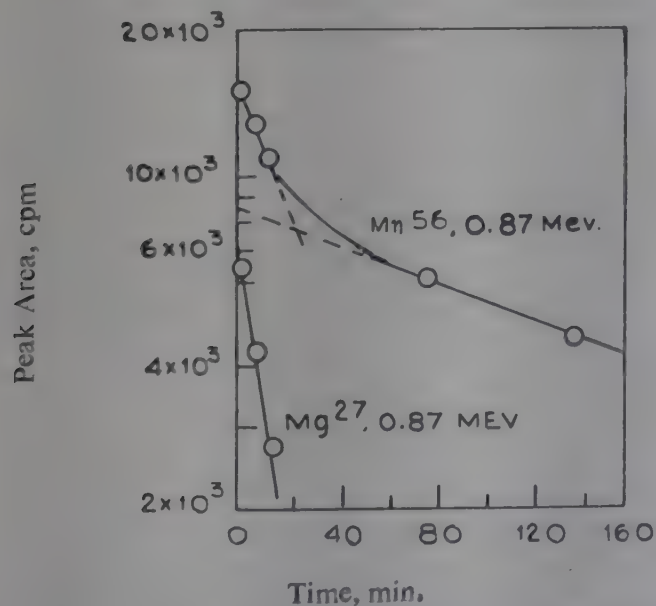


Fig. 4—Half-life Determination of Mn^{56} and Mg^{27} (Sample 1)
[Observed $T_{1/2}$: Mn^{56} 2.5 hr; Mg^{27} 9.0 min]

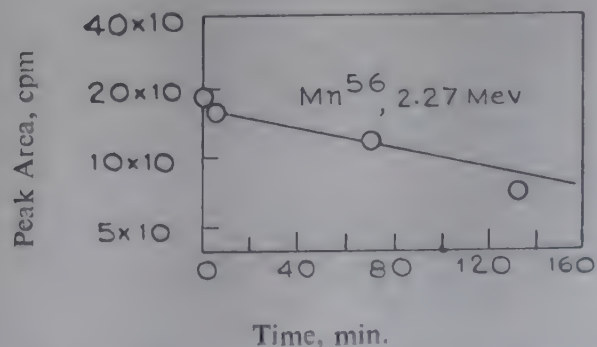
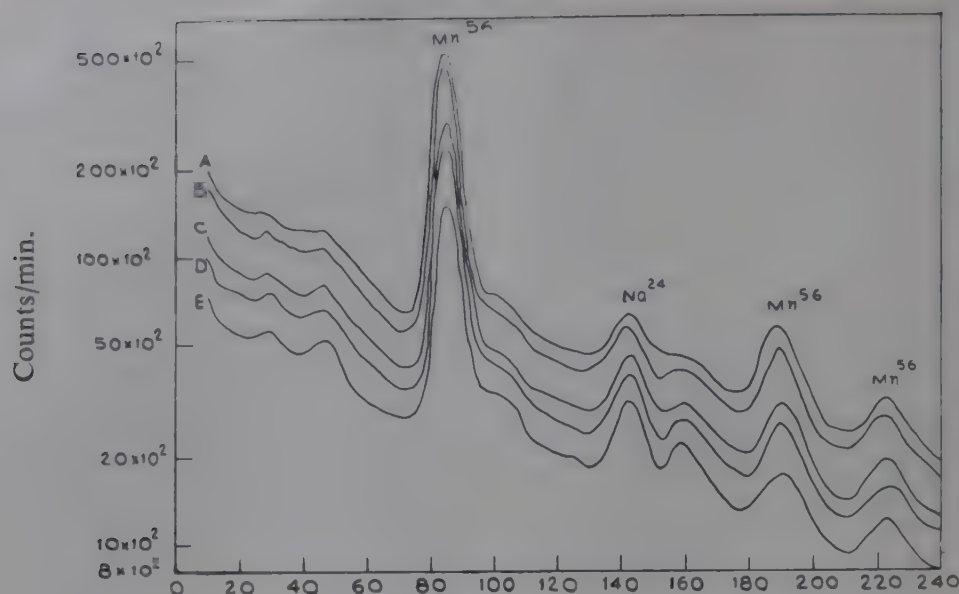


Fig. 6—Half-life Determination of Mn^{56} (Sample 1)
[Observed $T_{1/2}$ = 2.37 hr.]



Channels, 10 Kev/Channel
Fig. 7—Decay Spectra of Sample 2

Timing/hr.
A = 0.0 D = 3.1
B = 0.5 E = 5.0
C = 2.2

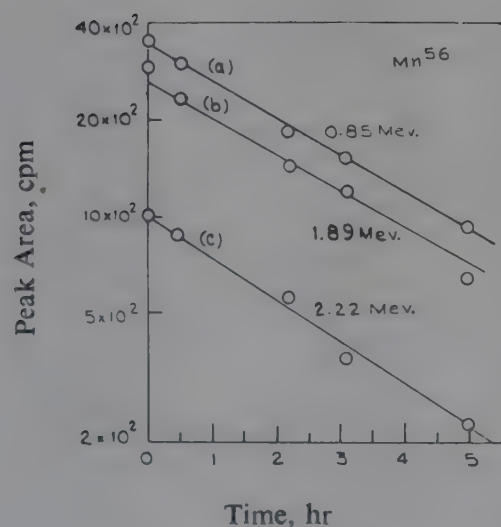


Fig. 8—Half-life Determination of Mn^{56} (Sample 2)

Observed $T_{1/2}$ = a. 2.5 hr
b. 2.6 hr
c. 2.4 hr

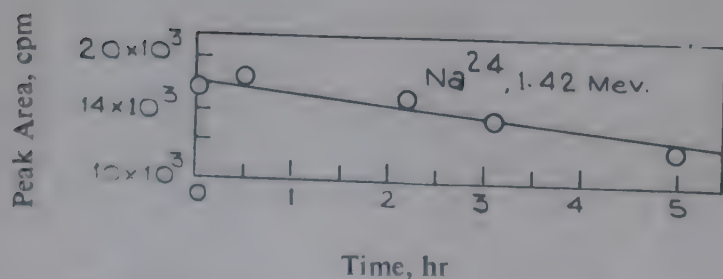


Fig. 9—Half-life Determination of Na^{24} (Sample 2)

[Observed $T_{1/2}$ = 15.2 hr]

The activity A of a sample irradiated by thermal neutrons is given by

$$A = \phi \sigma n (1 - e^{-0.693t/T_{1/2}}) \quad (1)$$

where ϕ is the neutron flux, σ the isotopic thermal neutron capture cross section, n the number of target atoms, t the irradiation time and $T_{1/2}$ the half-life of the radionuclide formed, all time-terms expressed in the same unit. If W be the weight of the sample, M the atomic weight of the element sought, f the fractional abundance of the isotope activated, and N Avagadro number, then the above expression assumes the form

$$A = \frac{\phi \sigma w f N}{M} (1 - e^{-0.693t/T_{1/2}}), \quad (2)$$

In the above expression, where the activity depends on elemental weight, the amount of the sought elements in an unknown sample can be readily found out by comparing its activity with that of the known weight of a standard, provided irradiation and counting conditions are kept strictly identical.

For a given element, if A_s and A_u represent the activity of the standard and the unknown sample respectively, then equation (2) reduces to

$$\frac{A_s}{A_u} = \frac{W_s}{W_u} \quad (3)$$

where W_s and W_u are the weights of the element in the standard and the unknown sample respectively. It is obvious from equation (3) that the percentage of the sought element in the unknown sample amounts to

$$\frac{W_s \times Au \times 100}{As \times W} \quad (4)$$

where W stands for weight of the sample taken.

By putting the experimental values of the variables in equation (4), the percentage of aluminium present in sample 1 becomes

$$= \frac{0.3865 \times 42371 \times 100}{638579 \times 1.6259} = 1.58 \quad (5)$$

Similarly, the percentage of manganese equals

$$\frac{0.1025 \times 126075 \times 100}{3144225 \times 1.6259} = 0.25 \quad (6)$$

The activity values of Al^{28} used in expression (5) were obtained after incorporating the necessary correction for the contribution of Mn^{56} . Similar correction were applied for Mg^{27} in the case of Mn^{56} (0.87 MeV). The quantitative estimation of magnesium in sample 1 and sodium and manganese in sample 2 is being worked out with the help of computer programming. To ascertain the presence or otherwise of iron an x-ray fluorescence spectrum was taken for sample 2 (Fig. 10). The FeK_{α} peak at 6.43 KeV is too obvious. This has been authenticated by comparison with spectrum of pure iron taken under identical conditions. A quantitative estimation of iron and other elements by XRF technique is in progress.

Acknowledgments

The authors' sincere thanks are due to Dr. A. K. Ganguly, Director, Chemical Group, Dr. M. R. Iyer

and Shri P. P. Chakraborty of Health Physics Division and to Shri Madan Lal of Nuclear Physics Division Bhabha Atomic Research Centre, Trombay, for extending experimental facilities and valuable help.

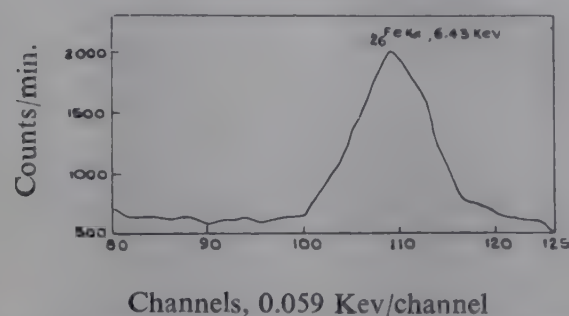


Fig. 10— I^{125} Excited X-ray Fluorescence Spectra of Sample 2

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While designing a storage system for bulk solids, some times it becomes necessary to plan a system which has a characteristic steady flow affecting the movement of all the stored bulk, and the flow region fully conforms to the container. These types of storage systems are generally called as 'Mass-flow' storage systems. By using the more defined flow properties of stored bulk solids, it is possible to design an optimum size bunker which can be a perfectly gravity flow type without any interruption to flow. A systematic procedure is suggested for the determination of optimum slope of hopper and its outlet size for a mass flow bunker or silo.

Design Procedure of Mass-Flow Bunkers and Silos

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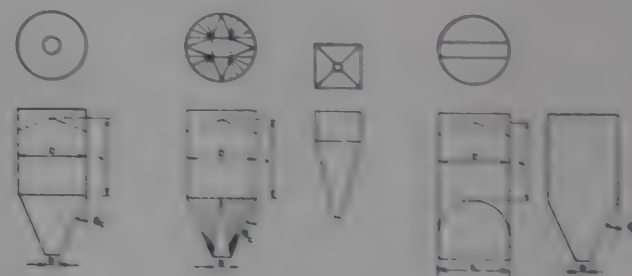
Introduction

In mass flow the contents in the hopper move at all points and sliding takes place at the walls whenever any solid is drawn through the outlet of the storage equipment. There are no inactive or dead regions in the stored mass. Mass flow is a gravity flow without any flow-promoting device. For selection of the storage to be designed as mass flow type, the following characteristics are necessary: (i) channeling, hang-ups, surging or flooding are absent, (ii) flow is uniform and a steady state flow is approached closely, (iii) pressures throughout the mass and at the walls are relatively low which results in a low consolidation or packing, (iv) there are no dead regions within the bin, hence there is a minimum of consolidation at rest, (v) a first-in and first-out flow patterns are obtained, if desired, which makes them useful in storage of solids which either deteriorate with time or segregate during charging into the storage and (vi) by circulating a mixture around a suitable bin, blending may be attained.

The mass flow storage equipments are designed to a variety of shapes (Fig. 1) as listed below: (i) bins or bunkers with conical or pyramidal hoppers (circular and square outlet); (ii) bins or bunkers with chisel hoppers (rectangular outlet or slot); (iii) the same with transition hopper (rectangular outlet); and (iv) the same with wedge hopper (full slot, or rectangular outlet).

The procedure adopted may be used for the design of the outlet size and the slope of the hopper portion of the storage equipment. The design assures a satis-

factory mass flow in the storage equipment without any dead region in the stored mass. It covers a variety of shapes under two distinct heads, viz. (i) conical channel with square or circular outlet, and (ii) plane flow channel with rectangular or full slot outlet.



(i) A—Conical (i) B—Pyramidal (ii) Chisel



(iii) Transition (iv) Wedge

Fig. 1—Mass Flow Bin Bunkers

Factors Influencing Design

Flow Properties of Stored Bulk Solids: The flow properties of the bulk solids stored in the equipment are the principal factors affecting the design. These

properties are determined under similar conditions of the bulk mass as it is stored in or delivered by the equipment being designed. The various factors affecting the flow properties are as follows : (i) particle size and shape, (ii) bulk density and consolidations, (iii) moisture content, (iv) temperature, (v) surface finish and storage equipment walls and (vi) period of storage. The flow properties, thus determined, help to get the outlet size, the slope of hopper and the load distribution on the walls of storage equipment.

Outlet Size : For a satisfactory flow in mass flow storage system, the outlet is required to be large enough so that plug-flow, piping, doming, etc. do not occur and the flow should continue without any flow-promoting device.

Slope of Hopper : For a good design the hopper slope angle is so selected that the stored mass moves in a first-in first-out fashion and each point of the mass moves when flow starts. The storage equipment should fully clear itself without any flow promoting device.

Lump Size : The flow is also influenced by lump size with respect to a certain outlet size. For uninterrupted flow out of a storage equipment the outlet is designed to an optimum size. Usually the lumps are free-flowing and suitable for mass flow.

Design Procedure

The size, unpacked bulk density of the powdered and granular solids, and the lump size were determined. The conditions of the bulk solid, like moisture content, temperature of the material of actual service and the period for which the material is stored at rest in the storage equipment along with the wall material equipment and its surface condition (finish and lining), were determined or the information was obtained from the storage equipment specification sheet.

The materials were tested on a shear tester (flow-factor tester) to obtain δ -distribution curve with respect to major consolidating force, V_1 and flow function, FF. The ϕ -distribution with respect to various consolidation was also determined and wall-yield locus was obtained experimentally¹. The values of shear cell area A , mean δ and ϕ' at the outlet conditions were determined from flow property data. ϕ' was estimated from WYL, (Fig. 2). δ and FF curves for coal are shown in Fig. 3.

(1) **Estimation of Hopper Slope :** The flow factor, ff, corresponding to the assumed δ and ϕ' values at outlet

were estimated from the figures showing ff contours for conical and plane flow channels^{2,3}. The ff values were so selected that the point (θ', ϕ') was very close to the extreme boundary. θ'_c was selected such that the point (θ'_c, ϕ') lies 3-5 degrees within the boundary of the selected ff for conical flow channels. In case of

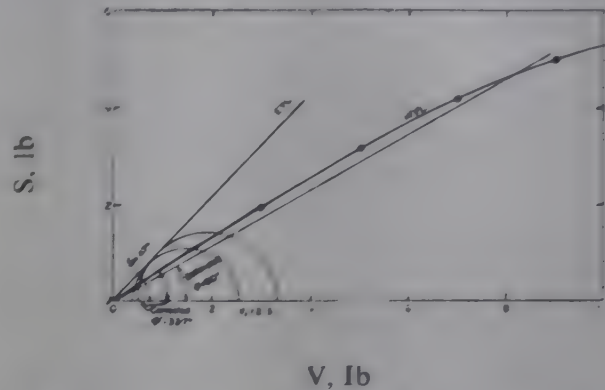


Fig. 2—Wall Yield Locus (Coal on Structural Steel)

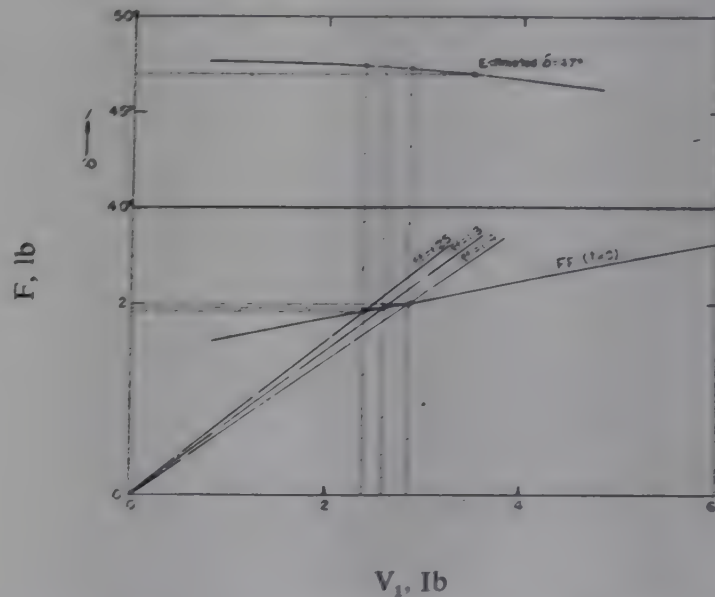


Fig. 3—Instantaneous Flow Function, FF(t=0) (Powdered Coal)

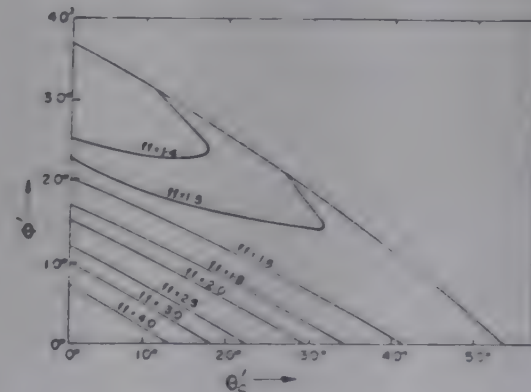


Fig. 4—Contours for Conical Channels, $\delta = 40^\circ$

plane flow channels, θ'_p was selected very close to the left of the dotted extreme boundary. In case of a smooth transition from vertical portion of storage equipment

to the hopper with a radius of curvature R^* greater than $D/3$, the θ_p' was increased by 5° than the optimum values selected earlier. Some of the ff contours are shown (Figs. 4-7).

(2) *Estimation of Outlet Size*: The estimated flow factor ff was plotted over flow-function FF (Fig. 3) of the bulk solids. FF was a plot of V_1 and F, whereas ff

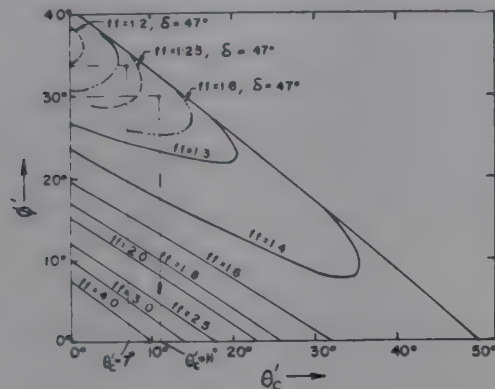


Fig. 5—ff Contours for Conical Channels, $\delta = 50^\circ$

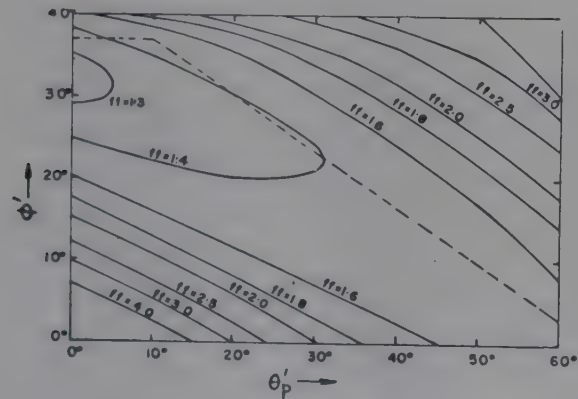


Fig. 6—ff Contours for Symmetric Plane-Flow Channels, $\delta=40^\circ$

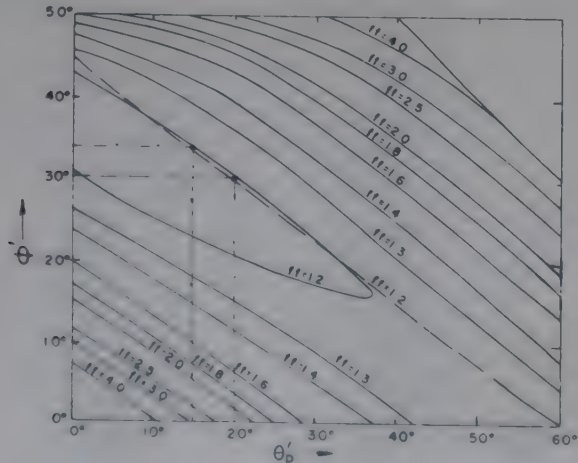


Fig. 7—ff Contours for Symmetrical for Symmetrical Plane-Flow Channels $\delta = 50^\circ$

* R is the radius of Curvature at transition, D is the diameter of vertical portion of storage System

was a plot of V_1 and $\bar{V}_1$ with V_1 as abscissa, the scale of the plots being same for both the factors. $H(\theta')$ corresponding to the estimated θ' for a selected shape of outlet can be determined from Fig. 8. Any one of the following alternatives may be faced during further analysis : (i) If there was no intersection of ff with FF and the latter lay below ff, it showed that the material stored was free-flowing and any dimension of outlet based on the rate of discharge and lump size would be sufficient. An outlet size B equal to 6 times the maximum lump size or the size based on discharge, whichever is greater, could be selected. $\bar{V}_1$ at the outlet condition was obtained by using the equation,

$$\bar{V}_1 = (B \gamma A)/H(\theta') \dots \dots \dots (1)$$

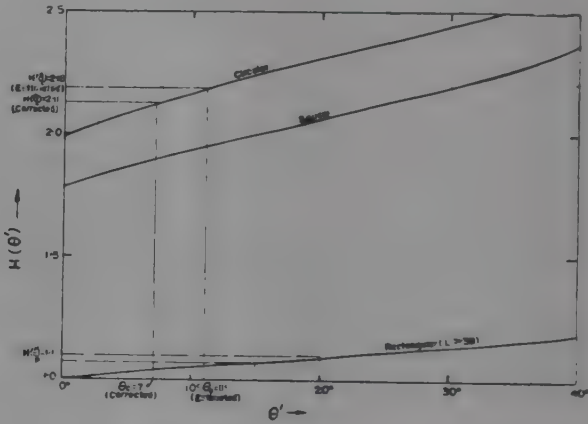


Fig. 8—Function $H(\theta')$

By locating the $\bar{V}_1$ on the ff line, V_1 at the outlet conditions was obtained, yielding $(V_1, \bar{V}_1)$.

(ii) If FF lay above ff it showed that the solid can not flow in a channel with flow-factor assumed. If lower values of ff were available and if an intersection of FF with ff were obtained based on this modified ff, the intersection point $(V_1, \bar{V}_1)$ was noted.

(iii) If there was an intersection of ff with FF, it showed that the storage equipment of a particular slope and outlet size could be designed for mass flow. The intersection points $(V_1, \bar{V}_1)$ were noted.

(iv) After plotting ff over $FF_{t=0}$ and FF_t , if it was found that the ff line lay between $FF_{t=0}$ but below FF_t , the stored material showed a tendency of consolidation with time. In these cases, vibrators were specified so that the flow can be started and the outlet was designed with a factor of safety to allow for unfavourable effect of vibrations. This could be accomplished by

selecting V_1 , so that at outlet, $\bar{V}_1=1.5 F$, which determines the point $(V_1, \bar{V}_1)$ in this case.

According to the cases encountered in design, a particular $\bar{V}_1$ and $H(\theta')$ were evaluated as described based on any modification in θ' values as derived earlier.

The minimum outlet dimension, B , could be calculated from the relationship $B=\bar{V}_1.H(\theta')/A \gamma \dots (2)$

Check for the Estimated Design Data: Corresponding to the V_1 value obtained during the estimation of the outlet size, δ could be read from the δ -distribution plot (Fig. 3). This δ -value determined the EYL of the stored mass at the outlet conditions. The Mohr's semicircle was drawn through $(V_1, 0)$ and tangential to EYL; the WYL was then drawn over this semicircle. The point of intersection determined ϕ' at outlet (Fig. 9), which were checked with the estimated ϕ' . If the estimated ϕ' did not tally with the checked value, a further estimation and modification of ff and δ were needed so that the checked value of ϕ' was closely reached to the corresponding estimated value. The recalculation for slope of hopper and outlet size should be done on the basis of the corrected data.

(4) *Adopted Design Values of Outlet Size and Slope of Hopper:* The hopper slope angles should be equal to or smaller than the calculated values, but not exceed in any case. In the case of conical hoppers or steep pyramidal hoppers the outlet should be circular or square. The diameter of circular outlet or the side of the square outlet should not be less than the calculated minimum dimension, B . In case of plane flow hoppers, the outlet should be rectangular or full-slot. If rectangular opening is adopted, the smaller side of the opening should not be less than 4 times (preferably 6 times) the maximum lump size. The greater side of this rectangular outlet should not be less than 3 times the smaller side ($L \geq 3 B$). In case of full slot opening, the width of opening was to be greater than the calculated B and it should accomodate 6 times the size of the maximum lump. The length of slot should be at least 6 times the width.

A sample calculation is shown in Tables 1 and 2. The sizes so obtained fix the overall system. The structural design should be based on the sizes fixed by this procedure. The load distribution on bunker and hopper walls which should be needed for the structural design will be communicated in a separate paper in the near future.

TABLE 1—DESIGN CALCULATION OF MASS FLOW SILOS, BUNKERS & HOPPERS (CONICAL-SQUARE/CIRCULAR OUTLET)

Bulk Material: Coal	Bulk size: —200 mesh. Lump size: Nil. Condition: Powdered, Moisture=6% (Air Dry). Average Bulk Density $\gamma = 40 \text{ lb./cu. ft.}$
Hopper Wall Material:	Structural Carbon Steel Finish—Medium.
Flow Properties of Bulk—material (Ref. Figs. 2 & 3)	Shear Cell Area, $A = 0.034 \text{ Sq. ft.}$ Estimated δ at outlet = 47 deg. Estimated ϕ' at outlet = 30 deg.
Estimated Hopper Slope Angle, θ_c'	
Estimated Flow-Factor (Ref. Fig. 5). ff	= 1.3
Slope angle θ_c' (Ref. Fig. 5 and stay $3^\circ\text{--}5^\circ$ within boundary)	= 11 deg.
Estimated Outlet Dimensions	
Estimate ff	= 1.3
$H(\theta')$ (Ref. Fig. 8)	= 2.18
Intersection of ff with flow function FF of Bulk Material (Ref. Fig. 3), $(V_1, \bar{V}_1)$	= (2.5, 1.9)
Minimum outlet Dimension, B	= $\bar{V}_1.H(\theta')/A \gamma \text{ ft.}$ 1.9×2.18 = $\frac{\quad}{0.034 \times 40} = 3.04 \text{ ft.}$
Corrected Outlet Dimensions	
V_1	= 2.5
Corresponding δ	= 47 deg.
By drawing Mohr's Semicircle through $(V_1, 0)$ & tangential to EYL & its intersection with WYL (Ref. Fig. 2), ϕ' at outlet	= 33.7 deg.
Corrected δ	= 47 deg.
Corrected ff (Ref. Fig. 5)	= 1.25
Corrected Slope Angle, θ_c' (Ref. Fig. 5)	= 7 deg.
$H(\theta')$ (Ref. Fig. 8)	= 2.11
$\bar{V}_1$	= 1.8 lb.
Minimum Outlet dimensions, B	= $\bar{V}_1.H(\theta)$ $\frac{1.8 \times 2.11}{0.034 \times 40}$ = 2.8 ft.
Adopted Values for Design	
Hopper Slope Angle, θ_c'	= 7 deg.
Outlet dimensions	= 2.8 ft. dia. (Circular outlet).

Table 2—DESIGN CALCULATION OF MASS FLOW SILOS,
BUNKERS & HOPPERS PLANE FLOW CHANNEL—(RECT-
ANGULAR/FULL SLOT OUTLET)

Bulk Material: Coal	Bulk size: = — 200 mesh. Lump size: = Nil. Condition: Powdered, Moisture = 6% (Air Dry). Average Bulk Density γ = 40 lb./cu. ft.
Hopper Wall Material:	Structural Carbon Steel Finish—Medium.
Flow Properties of Bulk Material: (Ref. Figs. 2 & 3)	Shear Cell Area, $A = 0.034$ Sq. ft. Estimated δ at outlet = 47 deg. Estimated ϕ' at outlet = 30 deg.
Estimated Hopper Slope Angle, θ_p'	
Estimated Flow Factor, ff (Ref. Fig. 7).	= 1.4
Estimated θ' (Ref. Fig. 7)	= 20 deg.
Estimated Outlet Dimensions	
Estimated ff	= 1.4
$H(\theta')$ (Ref. Fig. 8)	= 1.1
Intersection of ff with flow function FF of Bulk Material (Ref. Fig. 3), ($V_1, \bar{V}_1$)	= (2.8, 2.0)
Minimum outlet Dimension, B	= $\frac{\bar{V}_1 \cdot H(\theta')}{A \gamma}$ ft. = $\frac{2.0 \times 1.1}{0.034 \times 40}$ = 1.62 ft.
Corrected Outlet Dimensions	
V_1	= 2.8 lb.
Corresponding δ	= 47 deg.
By drawing Mohr's Semicircle through (V_1, O) & tangential to EYL & its intersection with WYL (Ref. Fig. 2), ϕ' at outlet	= 33.7 deg.
Corrected δ	= 47 deg.
Corrected ff (Ref. Fig. 7)	= 1.4
Corrected Slope Angle, θ_p' (Ref. Fig. 7)	= 15 deg.
$H(\theta')$ (Ref. Fig. 8)	= 1.08
$\bar{V}_1$	= 2.0 lb.
Corrected Minimum Outlet Dimensions, B	= $\frac{\bar{V}_1 \cdot H(\theta')}{A \gamma}$ = $\frac{2.0 \times 1.08}{0.034 \times 40}$ = 1.59 ft.
Adopted Value for Design	
Hopper Slope Angle, θ_p'	= 15 deg.
Outlet Dimensions, ($B \times L$)	= (1.6 $\times$ 4.8) ft. (Rectangular with $L \geq 3B$).

Nomenclature

γ	Bulk density (average of packed and aerated solid), lb./Cu. ft.
A	Shear Cell area (Cross-sectional area of test sample), Sq.ft.
δ	Effective angle of friction of bulk solids, degree.
ϕ'	Kinematic angle of friction between solid and the wall, degree.
θ'	Hopper slope measured from vertical, degree.
θ_c'	Conical hopper slope measured from vertical, degree.
θ_p'	Plane-flow hopper slope measured from vertical, degree.
V_1	Major consolidating force, lb.
$\bar{V}_1$	Major force in a dome or a pipe (Bulk-material under flow.), lb.
F	Unconfined yield force of bulk solid, lb.
B	Minimum Minor-dimension of opening, ft.
ff	Flow-factor of a channel (hopper), ($V_1, \bar{V}_1$).
$H(\theta')$	A function depending on θ' .
FF	Flow-function of bulk solid, V_1/F .
$FF_{t=0}$	Instantaneous flow-function of bulk-solids.
FF_t	Time flow-function of bulk solid stored for a period, t before delivery starts.
EYL	Effective yield locus of the flow of bulk-solid.
WYL	Wall Yield locus of the flow of bulk solid over a particular hopper wall.

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Concrete is being used more and more for making structural members in fertilizer plants. Corrosion of the concrete members and their protection in the aggressive environment of various chemicals are important from the point of view of the structural safety of the members. An attempt has been made here to critically analyse the parameters involved in concrete corrosion occurring in fertilizer industry and to delineate the optimal methods of protecting concrete. Repair of damaged concrete members has also been considered.

Protection of Concrete Structures in Fertilizers Industry

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Concrete, being a versatile construction material, is frequently used in fertilizer plants for making structural members like foundations, floors, columns, staircases, beams and roofs. These members are exposed to various aggressive chemicals including corrosive fumes, spillages, dusts, etc. One of the limitations of concrete is its vulnerability to attack by many chemicals. Since the structural safety is of utmost importance, protection of concrete structural members is an important determinant to be considered during designing as also in the maintenance.

With the rapid growth of fertilizer industry in the country during the last few years, concrete is being used more and more for structural purpose in the plants. The fertilizers at present manufactured in India include urea, ammonium salts of hydrochloric, sulphuric, nitric and phosphoric acid, some of their calcium and potassium salts and the soluble salts of some of these compounds. Their manufacture involves handling of gypsum, ammonia, sulphuric, nitric, phosphoric acids and corrosive gases, in addition to the already mentioned fertilizer chemicals.

Protection of concrete structure in a fertilizer plant requires a clear understanding of (a) the parameters involved in the deterioration of concrete in aggressive environment existing in the plant (b) preventive measures necessary for protecting the concrete and (c) the repair of the damaged concrete structures.

Durability of Concrete

Durability of concrete and concrete structures has two principal aspects, viz. (a) physical durability which is expressed as the loss of its mechanical and physical properties to an extent below the minimum required for structural safety and (b) economic durability which follows from the total cost expended in its building and maintenance. The cost¹ can be expressed by the following equation :

$$N = N_i + N_u + P_r S + N_1$$

where N = Total cost; N_i = Primary investment cost; N_u = Total maintenance cost; P_r = Probability that the structure will collapse in time T_r ; S = Material damage caused by the structure collapse; and N_1 = The cost of tearing down and removing the structure.

The economic durability is given by $\frac{\delta N}{\delta T} = 0$ Saving in the investment cost usually leads to higher total maintenance cost of the structure.

The action of aggressive agents on concrete depends on (a) their nature, concentration and extent of contact and (b) properties of concrete and its ingredients in relation to the aggressive agents.

Nature of the Aggressive Agents: Most of the chemicals that are being handled in various fertilizer manufacturing units are highly corrosive towards fresh and hardened concrete. The ammonium salts of nitric, sul-

phuric, phosphoric and hydrochloric acids are much more deleterious to concrete than the corresponding alkali and alkaline-earth salts. The formers react with the free lime liberating ammonia and forming calcium salts of the corresponding acids, e.g.



The same reaction also takes place if the anion is nitrate, sulphate or phosphate instead of chloride. This makes the lime of the concrete to be leached out and the action is similar to free mineral acids. Table 1 shows the effect of various fertilizer chemicals on hardened concrete. While slag cement, pozzolana and high alumina cement concretes show good resistance towards the alkali and alkaline-earth salts of the mineral acids mentioned previously, even the most resistant high alumina cement concrete quickly disintegrates when placed in environment containing corresponding ammonium salts.

Properties of Concrete in Relation to the Agents: An adverse effect is given by permeability, porosity, moisture absorption, reduced bond between cement and aggregate and the tensile strength of concrete. These properties are controlled by cement quality, proportioning, grading of aggregates, compaction and curing of concrete. Of all these, cement quality compaction and grading of aggregates has considerable contribution towards the variability in concrete quality. Non-homogeneity in concrete leads to stress concentration in stronger part and chemical attack on the weaker part of the concrete. Inadequate curing schedule leads to more of shrinkage cracks. The code of practice takes care of these determinants and spells out directions for making sound concrete².

The cracks and their formation are of decisive importance. While cracks are inherent characteristics of hardened concrete, they can be appreciably reduced by adopting optimal procedures² and use of prestressed concrete members results in absence of cracks in most circumstances.

The construction joint is one of the most vulnerable point of attack and special care should be taken in case of RCC work because of chance of reinforcement corrosion.

Protection Measures

The protection of concrete members against intensive contact of the aggressive media is the cheapest solution of the durability problem. The protective measures can be (a) adjustment of the environment to the structure and (b) treatment of concrete and concrete surfaces.

Adjustment of Environment: It involves preventing or diluting the contact of the aggressive media with the concrete, ventilation or withdrawal of aggressive vapours and gases, weakening of the agents by dilution or neutralization and conveying the agents through proper drainage. In most of the plants, it may not be possible to effect a total absence of aggressive media and as such protection of concrete in the way of its treatment is necessary. The use of special ingredients for concrete-making, treating it with chemicals or coating it with corrosion-resistant materials are the treatments generally adopted.

Treatment of Concrete: A rich and dense concrete is inherently resistant to many corrosive agents. A 270 kg./m³ cement concrete is about 10 to 20 times more resistant to chemical attack than a 150 kg./m³ cement concrete³. However, no concrete can stay unattacked when a protonic dissolution (acid attack or action of ammonium salts) takes place.

The concrete can be protected by treating it or its surface with various chemicals and by applying corrosion resistant paints, coatings, mortars or cladding on its surface. Concrete surfaces are treated with magnesium or zinc silico-fluoride or silicon tetrafluoride gas. The latter treatment is called 'Okrat process', where the concrete member is exposed to silicon tetrafluoride gas under pressure. The gas enters deep into the pores and precipitates silica gel by reacting with the lime thus sealing the pores. The Okrated concrete is fairly resistant to even mild acid attack and is excellently resistant to relatively less corrosive agents.

The coatings on concrete usually are various organic polymer materials, but inorganic cements, ceramics and metals are also used. Table 2 gives a classification⁴ of these protective barriers. The choice of the material for protection depends on (a) the nature of the attacking agent (b) degree of attack and (c) the sanctioned expenditure on the protection job. Table 1 shows the coatings and mortars normally recommended against the attack of fertilizer chemicals. Table 3 shows the engineering properties of some typical chemical resistant mortars in usage. Table 4 gives the details regarding some of the chemical-resistant barriers including their limitations and cost.

Maintenance of Concrete Structures and Repair of Damaged Concrete

Maintenance and repair of concrete structures are important factors in both physical and economic durability. The task of systematic maintenance consists in ensuring for a structure the same conditions as have

TABLE 1—EFFECT OF CHEMICALS ON HARDENED CONCRETE AND RECOMMENDED PROTECTIVE BARRIERS⁴

Chemicals	Effect on Hardened Concrete	Protective Barriers Recommended			Abbreviations Used
		Thin Coating	Thick Coating	Mortar	
1. Ammonia	May Disintegrate Moist Concrete	Btmn, PE, Vn	Btmn, Vn, Bk, Tl	Fu, PE, Ep, Asph	As: Sodium or Potassium Silicate
2. Ammonium chloride, nitrate, phosphate sulphate	Disintegrate Concrete	Btmn, Ep, Neo, PE SBD-R, Vn, As	Btmn, Vn Neo	Fu Ph, S, E, PE	Asph: Asphalt Bk: Brick Btmn: Bitumen, Cl-R chlorinated rubber
3. Nitric & other mineral acids	Rapid disintegration	As, Cl-R, Ep Neo Vn	Bk, Tl, Btmn, Vn, PE	S, PE	Ep: Epoxy Fu: Furan Mg/Zn SiF ₆ :
4. Calcium nitrate	Not harmful	As, Neo, PE, Vn, Mg/Zn SiF ₆	Bk, Tl, Btmn, Vn, Neo	Fu, Ep, S	Fluo Silicate of Magnesium or Zinc
5. Calcium Sulphate	Disintegrates concrete of inadequate sulphate resistance	Sulphate resisting cement concrete with As, Neo, PE, Vn, SBD—R	Bk, Tl, Btmn, Vn, Neo	Fu, Ph, S	Neo: Neoprene PE: Polyester Ph: Phenolics S: Sulphur SBD-R Styrene
6. Urea	Not harmful	Ep, Neo, Vn	Bk, Tl, Btmn, Neo, Vn	Fu, Ep	Butadiene rubber Tl: Tile Vn: Vinyls

TABLE 2—CLASSIFICATION OF PROTECTIVE BARRIERS⁴

Protective Barriers					
Thermoplastic Resin	Thermosetting Resin	Inorganic Surface Treatment	Ceramics	Mortars	Sheet Materials
(a) Wax and greases	(a) Drying oils	(a) Silicates	(a) Bricks	(a) Sulphur	(a) Rubber sheet
(b) Bituminous & Latex emulsion	(b) Alkyd	(b) Fluosilicates	(b) Tiles	(b) Silicates	(b) Resin sheet
(c) Bitumen	(c) Phenolics	(c) Silicon tetrafluoride		(c) Phenolics	(c) Lead sheet
(d) Rubber or resin	(d) Epoxies			(d) Furans	
(e) Vinyls	(e) Urethanes			(e) Polyesters	
	(f) Neoprenes			(f) Epoxies	
	(g) Polyesters				
	(h) Furans				

TABLE 3—ENGINEERING PROPERTIES OF SOME TYPICAL CHEMICAL RESISTANT MORTARS⁴

Properties	Sulphur	Silicate	Phenolics	Furan	Polyester	Epoxy	Concrete (200 kg/cm ² after 28 days)
1. Density, kg./m ³	2208	2000	1690	1520	2000	1520-2000	2400
2. Apparent Porosity, %	<1	>12	<1	<1	<1	<1	8
3. Tensile Strength, kg./cm ² .	42	24.5	84	98	98	112	21
4. Compressive Strength, kg./cm ² .	420	245	700	840	840	1120	200
5. Modulus of Elasticity, kg./cm ² . × 10 ⁴	8.4	7.0	4.2	7.0	10.5	9.1	28
6. Modulus of Rupture kg./cm ² .	98	52	98	112	122	126	21
7. Coeff. Linear Expan., cm./cm. C × 10 ⁻⁶	33	11	15	21	32	25	11
8. Max. Service Temp., °C	95	350-800	160	160	120	120	—
9. Working Time of Mixed Mortar at 30°C	—	40	30-120	30	60	45	—
10. Final Setting Time, day	—	3	3-4	2	2	2	Varies depending on mix & environment.
11. Linear Shrinkage, %	—	1.0	0.8	0.4	1.2	0	

TABLE 4—DETAILS OF SOME CHEMICAL RESISTANT BARRIERS

Barrier	Nature	Application Method	Concrete Condition and Treatment Required	Effectiveness	Disadvantages	Type of Coating	Approximate Cost/sq.m. Rs.
1	2	3	4	5	6	7	8
1. Asphalt	Mastic or plasticized coaltar	Hot or cold or cold solution	Dry concrete primer may not be required depending on the product	Good	Colour limitation, softens at elevated temperature, poor resistance to solvent	Thick or mortar	3/-
2. Bitumen	Emulsion	Cold	Dry concrete surface clean, Primer may or may not be necessary depending on the product	Fair to good	Comparatively high permeability, poor resistance to solvents	Thin or thick	25/-
3. Alkali Silicate	Aqueous solution	Cold	—	Fair	Soluble in water quickly washed away if hosed	Thin coating	2/-
4. Mg/Zn Fluosilicate	Aqueous solution	Cold	—	Fair	Quickly washed away by hosing	Thin coating	3/-
5. Polyester	Two pack resin contains resin & hardner re-active diluent available	Cold premixed	Concrete surface clean & grease free	Very good	Careful control of catalyst or hardner required. Excellent finish is a must	Thin, thick or mortar	Data not available but fairly costly
6. Neoprene	One pack or two packs resin	Cold	Concrete surface clean & grease free	Very good	Swell severely by aromatic hydro carbon, Poor resistance to strong oxidising media	Thin or thick	Data not available but fairly costly
7. Chlorinated rubber	Solid resin plasticizer stabilizer system	Cold	Clean and grease free concrete surface Primar generally not needed	Very good	Not resistant to nitric acid and concentrated ammonia. Attacked by oil & solvents	Thin and thick	35/-
8. Epoxy	Two pack resin hardner system	Cold	Clean and grease free concrete surface	Excellent	Not very resistant to strong nitric acid	Thin, thick or mortar	50/-
9. Vinyls	One pack system solution in solvent or latex emulsion	Cold solution	Clean grease free concrete surface	Excellent	Some formulations attacked by very hot water or steam, low solid content. Difficult to overcoat. Poor bond to concrete	Thin and thick	Data not available
10. Sulphur	Hot melt	Hot	Dry clean grease free concrete surface	Very good	Difficult to work with very low pot life can be used best as a jointing material in laying bricks and tiles	Mortar	50/-
11. Bricks and tiles	—	—	—	Excellent	Good workmanship required for making sealed joints	Cladding material	200/-
12. Phenolics	Liquid resin catalyst, inert filler system	Cold	Concrete surface dry clean and grease free	Very good	Low shelf life. Hazard to skin poisoning. Attacked by strong oxidizing agents	Mortar	Medium costly
13. Furans	Two package resin and filler catalyst mix	Cold	Dry clean and grease free concrete surface	Very good	Short working time	Mortar	Medium costly

been considered in design. The maintenance includes systematic checking of loading, environment and the condition of the concrete member under load including the nature and extent of the cracks and adjusting the parameters for optimum. Proper drainage of water and effluents is one such step for optimization.

The object of repair is to stop the progress of deterioration and to restore the structure to its original safety. It is essential to establish the extent of damage and to determine if the major portion of the structure is suitable for repair. The efficiency of the repair is considerably dependent on the quality of bond between the old and the new concrete. Preparation of concrete surface is the major determinant in achieving the bond. It includes complete removal of defective concrete, bringing out a sound concrete surface and drying of the surface.

Shot-creting: Shot-creting is well adopted for concrete repair, specially in case of complex shaped members, vertical members, roof and when there are closely spaced reinforcements. This methodology of repair ensures better bond between old and new concrete and the durability and strength of the shot-creted concrete are comparable to the conventional concrete repair⁵. Shot-creting is not preferred when the repair work is more than 7 to 10 cm. thick⁵. Failure of shot-created concrete is mainly due to improper surface preparation and use of substandard materials. The shot-creting is relatively expensive than conventional concrete. The cost of former is about Rs. 500-1000/m³ against Rs. 400-600/m³ for the latter.

Epoxies in Bonding Old and New Concrete: Epoxies have eased the problem of bonding old and new concrete in a repair work. An epoxy primer coating on the prepared old concrete surface excellently binds the new concrete to the old one. Epoxies have high tensile and compressive strength, high modulus of elasticity and extremely low shrinkage. The creep of the resin formulation can be tailor-made to some extent. The differential expansion (thermal) between concrete and epoxies can be adjusted with epoxies of desired creep. Epoxies are costly but ensures excellent results and application procedures have already been standardized⁶. The epoxy formulation should be thixotropic so as to be able to hold at least 15 mm. without sagging. The placement of concrete is delayed for sometime till the film is tacky to the finger. With vibrator the degree of tack should be more.

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A study has been made to see the effect of four different organic acids, viz. crotonic, stearic, succinic and malic acids (at 0.4 per cent concentration), on the fixation of phosphate by soils under three different moisture treatments in aqueous media at 30°C. It has been found that organic acids increase the phosphate fixation irrespective of soil type and treatments given to them. Generally, maximum phosphate fixation has been observed by alluvial soil in presence of stearic and malic acids and red and alkali soils in presence of crotonic and succinic acids and also with high initial soil moisture (treatment A) condition. However, in certain cases, especially in case of low soil moisture (treatment C), red and alkali soils record enhanced phosphate fixation.

Fixation of P_2O_5 by Soils in Aqueous Medium in Presence of Some Organic Acids

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Introduction

It is a well-known fact that organic substances in general reduce phosphate fixation by soils¹⁻³. This is said to be due to the saturation of the active spots on the soil surface by the organic substances which would otherwise have been the centres of phosphate fixation. It is, therefore, felt that it would be worthwhile to see the effect of certain common organic acids, viz. stearic, crotonic, succinic and malic, on the fixation of phosphate by five typical Indian soils in aqueous media at 30°C under three different moisture treatments. The maximum fixation of P_2O_5 by soils has been obtained with 0.4 per cent concentration of these acids the study has, therefore, been confined with this concentration only.

Experimental

Five typical Indian soils from a depth of 0-15 cm. were collected. The soils were then dried, pulverized and finally passed through 100 mesh (BSS) sieve. These were then analysed for their different physico-chemical properties².

For observing the effect of different organic acids on phosphate fixation, the following three different treatments were given to each soil sample :

Treatment A : consists of high initial soil moisture,

Treatment B : of moderate soil moisture

Treatment C : denotes low initial soil moisture in comparison to treatments A and B.

For each treatment, 10 g. soil was taken in plastic dishes and treated with 0.4 per cent of each of the organic acids, viz. stearic, crotonic, succinic and malic, in aqueous medium at 30°C and kept for one month. A measured amount of distilled water, viz. 15, 10 and 5 ml. per 10 g. soil, was added in treatments A, B and C respectively. After the lapse of the experimental period, the soils were dried, pulverized in an agate mortar and kept in oil paper bag to perform the experiment.

5 g. of the above treated soil was taken in a 100 ml. volumetric flask and a required volume of 50 mg. of P_2O_5 in the form of phosphoric acid (H_3PO_4) was added and the remaining volume was made upto the mark with distilled water. The contents were mixed, properly shaken and allowed to stand for 24 hours. Next day, 5 ml. of the supernatant liquid was taken and analysed for phosphorus colorimetrically,^{5,6} using 660 m μ red filter.

The pH values were taken⁷ by Phillips pH meter. The initial pH values of the treated soils were taken just after the addition of different organic acids whereas the final pH values of the treated soils were taken after the incubation period.

The difference between the P_2O_5 added and the P_2O_5 remained in solution was taken as the amount of P_2O_5 fixed* by soils at different conditions.

*The words fixation, retention or adsorption are used here synonymously.

TABLE 1—SOME PHYSICO-CHEMICAL PROPERTIES OF SOILS

Soil	Place	Properties					Texture	Nature of Predominant Clay Minerals
		Total R_2O_3 , %	Total Al_2O_3 , %	Aver. P_2O_5 , %	Organic Matter, %	pH		
1. Black Cotton	Krishna Distt. (A.P.)	21.33	12.15	0.0008	1.64	7.50	Clay	V, M
2. Laterite	Coimbatore (Tamil Nadu)	9.47	5.32	0.0044	1.34	6.1	Loam	V, K
3. Alluvial	Allahabad (U. P.)	3.58	4.90	0.0107	0.93	7.5	Loamy sand	I, M
4. Red	Ranchi (Bihar)	16.95	10.32	0.0034	1.52	5.3	Sandy clay loam.	K
5. Alkali	Allahabad (U. P.)	7.15	4.46	0.0072	0.55	10.4	Sandy-loam	M, I

* 1. V=Vermiculite; M=Montmorillonite; K=Kaolinite; I=Illite.

2. The above clay minerals in the soils were identified by x-ray method.

TABLE 2—FIXATION OF P_2O_5 BY SOILS IN AQUEOUS MEDIUM IN PRESENCE OF 0.4% ACIDS AT 30°C
mg. of P_2O_5 added/100 g. soil = 100 mg.

P fixed/100 g. soil, mg.			Initial pH			Final pH		
Treatments			Treatments			Treatments		
A	B	C	A	B	C	A	B	C
(i) Stearic Acid								
1. 50	100	80	5.6	6.3	6.6	6.8	6.6	6.7
2. 20	160	80	4.8	5.4	6.2	5.0	6.1	6.1
3. 350	260	100	5.0	4.6	5.5	4.2	5.5	5.8
4. 250	40	40	4.6	4.4	5.8	4.2	5.5	6.1
5. 300	160	—140	6.0	6.6	7.1	6.9	6.9	7.4
(ii) Crotonic Acid								
1. —150	160	160	5.6	6.3	6.6	6.6	6.2	6.5
2. 50	80	160	4.8	5.4	6.2	4.6	6.0	5.0
3. 0.00	160	260	5.0	4.6	5.5	4.2	5.4	4.4
4. 300	100	20	4.6	4.4	5.8	4.2	5.5	4.3
5. 200	240	40	6.0	6.6	7.1	6.4	6.9	6.8
(iii) Succinic Acid								
1. —50	100	80	5.6	6.3	6.6	6.0	6.8	6.6
2. 0.00	—810	0.00	4.4	5.4	6.2	5.4	6.2	5.8
3. 100	140	200	5.0	4.6	5.5	4.2	5.4	4.4
4. 140	40	100	4.6	4.4	5.8	4.2	5.3	4.4
5. 100	180	120	6.0	6.6	7.1	6.4	6.9	6.8
(iv) Malic Acid								
1. —150	260	140	5.6	6.3	6.6	6.2	6.7	6.4
2. 0.00	40	240	4.8	5.4	6.2	4.4	6.0	6.0
3. 350	320	100	5.0	4.6	5.5	4.2	5.4	4.4
4. 150	160	80	4.6	4.4	5.8	4.2	5.6	4.2
5. 200	280	60	6.0	6.6	7.1	6.2	6.9	7.0

The values given in Table 2 (i to iv) indicate the difference of values between those obtained in presence of the treatments and control.

Results and Discussion

A perusal of Table 2 (i to iv) clearly indicates that, in general, the fixation of phosphate is increased in presence of all the organic acids irrespective of the different soil treatments and conditions. When phosphate solution and organic acids are added together under a high moisture supply (Treatment A), the alluvial soil (loamy sand texture) in presence of stearic and malic acids and red soil (sandy clay loam) in presence of crotonic and succinic acids records the maximum enhanced phosphate fixation.

Further, Table 2 (i to iv) indicates, that in general, in presence of stearic and crotonic acids, all soils record the maximum enhanced phosphate fixation with initial soil moisture (treatment A), and this is with malic and crotonic acids with average soil moisture treatment B and with limited soil moisture (treatment C) conditions. In some cases, especially in the case of treatment C, red and alkali (sandy loam) soils record enhanced phosphate fixation in presence of succinic acid. In treatment A, similarly, black cotton and laterite soils record enhanced phosphate fixation in presence of succinic acid. Generally, for all soils maximum enhanced phosphate fixation in presence of organic acids is recorded under treatments B and C. However, in case of alluvial, alkali and red soils and in presence of stearic acid, maximum enhanced phosphate fixation appears to be favourable under treatment A (high initial soil moisture) condition.

Enhanced phosphate fixation is generally accompanied by an increase in the resultant pH, especially under treatment B condition. In other cases, phosphate fixation is accompanied by a decrease in pH. The following explanations may be forwarded for elucidating enhanced phosphate fixation in the presence of organic acids.

It is well-known that phosphoric acid will dissociate into different phosphate ion species and thereby release

hydrogen ions according to the pH of the system. The H^+ ion will react with soil aluminium releasing considerable amount of active aluminium from the lattice to the exchange positions. The organic acids will also dissociate and release H^+ ions which in its turn will move lattice aluminium to the surface. The anions of the organic acids will get attached to the Al^{3+} ions of the soil surface due to electrostatic forces and the aluminium phosphate ion so produced will take position in the soil, liberating corresponding amounts of H^+ ions, thus lowering the resultant pH.

The increase in the resultant pH by the soils in presence of different organic acids is probably due to the fact that H^+ ion (released from phosphoric acid as mentioned above) will obviously activate more soil and precipitate insoluble aluminium phosphate on the soil surface. This means that due to the release of Al^{3+} ions, the electronegativity of the surface increases and this is neutralized by the H^+ ions of the solution resulting in an increase of the resultant pH. These H^+ ions will also be neutralized by reacting with OH^- ions released from the soil colloid clay minerals as a resultant of their exchange with $H_2PO_4^-$ ions present in the solution.

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Analysis of 16 soils from different locations of Ranbir Singhpora tehsil, Jammu district, in respect of physico-chemical and microbiological properties indicated (1) their heavy texture except Kharian ; cation-exchange capacity from 6.17 to 10.20 m.e. % and exchangeable cations, viz. calcium, magnesium, potassium and sodium from 3.08 to 6.30, 0.27 to 2.26, 0.41 to 1.88 and 0.23 to 3.00 m.e. % respectively ; (2) pH, electrical conductivity, organic carbon and total nitrogen were recorded from 6.1 to 9.5, 0.2 to 4.66 mmhos, 0.22 to 1.00 per cent and 0.02 to 0.11 per cent respectively ; (3) available nitrogen and phosphate (P_2O_5) ranged from 5 to 20, 2.1 to 6.9 mg./100 g.; and (4) all the soils revealed the presence of *Azotobacter*, the total bacterial population was high in neutral and slightly alkaline soils, fungi were dominating in acidic soils and actinomycetes were higher in alkaline ones.

Studies on Certain Physico-Chemical and Microbiological Properties of Ranbir Singhpora Soils of Jammu & Kashmir

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Ranbir Singhpora tehsil of Jammu district in the State of Jammu & Kashmir is agriculturally very important. Out of its total area of 401.5 square kilometers, about 324 square kilometers are under cultivation. Basmati paddy known for its superior quality, along with its high-yielding varieties, viz. China-1039 IR-8, Palaman etc., thrive best here. Earlier to this investigation, no detailed studies of this area had been made. In the present paper, some of the physico-chemical and microbiological properties have been investigated to fill up the lacuna.

Description of the Area

Ranbir Singhpora tehsil is located at 74.8°E latitude and 32.5°N longitude, bounded by the *Balwal* and the *Tawi* rivers in the north, by the Samba tehsil in the East and by the Indo-Pakistan borders in the South and West. In topography, it is generally flat but has low-lying areas in the South-West portion, which is alluvial with silt brought by *Tawi*. The climate is sub-tropical with extremes of high summer and winter. The annual rainfall is about 1000 mm., which is confined to a few months from July to September. Three major streams, called the *Aik*, *Balwal* and *Palkhu*, with many perennial and intermittent small streams drain the entire area. The whole of the tehsil is irrigated by the Ranbir Canal. The water table is approximately 2 metres depth.

Experimental

16 surface soils (0-22.5 cm. depth) were collected from different places of the tehsil. Initially, they were air dried and passed through 10 mesh (Bss) sieve. For their analysis, the standard methods were adopted. The populations of each kind of micro-organisms was determined by the standard plate-counting method in soil dilution of suitable range. For each dilution, three plates were used and the average count made. Thornton's, Jenson's, Martin's and Burk's media were employed to determine bacteria, actinomycetes, fungi and *Azotobacter* as described by Allen⁴. Morphological groupings of the microfloral isolates were done by microscopical examination of the culture characteristics, as described in the Manual of Microbiological Methods⁵.

Results and Discussion

Mechanical composition, cation-exchange capacity and exchangeable bases are presented in Table 1. The data shows that the majority of the soils studied are clay loam and loam in texture. Out of these soils one belongs to the textural class sandy loam (Kharian), one to clay (Barley) and two silty loam (Bishnah, Darso-pur). Two soils have been found to contain more of coarse sand (15.4 to 20.6 per cent) but even then they belong to clay loam and clay respectively. Cation-

exchange capacity varies from 6.17 to 10.2 m.e. % showing maximum in Barlley soil and minimum in Kharian. Fine texture and organic carbon content of these soils appear to have influenced these values. Almost in all the soils, more than 50 per cent of exchangeable calcium of the total exchange capacity has been observed. Exchangeable magnesium varies between 0.27 and 2.6 m.e. %, which appears to be the second major cation in these soils. It may be due to the presence of chlorite type of clay minerals in addition to illite types, as observed by Gupta⁶.

Exchangeable potassium was found to lie between 0.41 and 1.88 m.e. against cation-exchange capacity of 6.17 to 10.20 m.e.% showing less than 5 per cent in five soils, viz. Kotli, R.S.Pura, Makhanpur, Tinde and Kharian, which are considered deficient in available or exchangeable potassium^{6,7}. This finding is at par with those of Mann and Sharma⁸ and Gupta⁹, who came to the same conclusion. Application of potassic fertilizer is therefore, essential to increase the availability of potassium for the growing crops in these soils. More than 15 per cent of exchangeable sodium has been seen in 3 soils (Mothey, Barlley and Bishnah), which is not within safe limits to the crops. Addition of gypsum is, therefore, recommended to reclaim these soils.

pH, electrical conductivity, total and available nitrogen, phosphate (P_2O_5), microbial population of bacteria, actinomycetes, fungi and *Azotobacter* have been shown

in Table 2. The pH of the soils is as high as 9.5 and as low as 6.1. Out of 16 soils, 3 are grouped in acid range (pH less than 6.5) and 6 in alkaline range (pH greater than 7.5), while the remaining ones are neutral in reaction. The alkaline reaction recorded in these soils may perhaps be due to high water table in this region, whereas cropping influence is attributable to acidic reaction because some soils were collected just after the harvest of paddy. Since the paddy fields remain under water-logged condition during most of their growth period, which increases the concentration of iron and aluminium and in turn produces acidity. The electrical conductivity varies from 0.20 to 4.66 mmhos/cm. showing great variations. It can be explained on the basis of continuous irrigation through Ranbir Canal to this area, which as a result makes the water table high. It is suggested that irrigational water should also be analysed to know its nature in respect of soluble salts the higher concentration of which may prove harmful to the crops.

Organic carbon and total nitrogen are found to be 0.22 to 1.00 and 0.02 to 0.11 per cent respectively. These values are very less as compared with the soils of inner zone of Jammu and Kashmir as investigated by Gupta^{6,9}. The effect of vegetation and climate may be applicable here to account these differences because the area under study belongs to the sub-tropical zone, the higher temperature of which enhances the decomposition

TABLE 1—MECHANICAL COMPOSITION, CATION-EXCHANGE CAPACITY AND EXCHANGEABLE BASES OF RANBIR SINGHPURA SOILS

Soil	C.S., %	F.S., %	Silt, %	Clay, %	Textural Class	C.E.C., m.e. %	Exchangeable Bases, m.e. %			
							Ca	Mg	K	Na
Narikhepar	0.5	47.0	23.8	30.2	CL	7.81	4.48	0.27	0.61	0.26
Gegian	0.2	49.0	23.4	28.2	CL	8.10	5.30	1.23	0.99	0.30
Kotli Shahdola	2.8	51.0	16.4	29.4	CL	7.71	4.50	1.28	0.71	0.85
Kharian	8.9	62.4	10.0	15.4	SL	6.17	3.67	1.28	0.41	0.48
Baggamarh	1.2	44.1	22.1	31.2	CL	6.66	4.00	0.80	0.75	0.45
Makhanpur	4.2	54.4	10.2	29.4	CL	8.30	5.40	1.10	0.41	0.66
Tinde	2.0	56.6	19.6	21.2	L	9.90	6.30	0.80	0.41	0.86
Miran Sahib	4.8	60.5	17.6	16.4	L	7.00	4.20	0.63	1.02	0.70
Purana Pind	15.4	32.1	19.0	32.2	CL	8.10	5.67	0.33	1.00	0.90
R. S. Pura	1.0	48.1	20.4	31.2	CL	8.20	6.17	0.90	0.41	0.23
Thikrian	7.5	40.0	21.8	32.2	CL	7.60	3.70	1.16	0.60	0.24
Kotli	3.2	64.7	14.6	16.6	L	7.55	3.08	1.18	0.41	0.43
Barlley	20.6	19.0	21.8	40.1	C	10.10	5.11	1.18	1.40	2.20
Bishnah	4.8	50.9	28.9	14.2	SIL	10.20	5.15	0.80	1.71	3.00
Darsopur	4.0	50.5	29.6	16.8	SIL	8.80	4.90	1.10	1.88	0.34
Mothey	4.8	51.2	23.1	20.0	L	9.95	5.10	2.26	0.47	2.35

C.S.—Coarse Sand; F.S.—Fine Sand; CL—Clay Loam; SL—Sandy Loam; SIL—Silty Loam; L—Loam.

TABLE 2—CHEMICAL AND MICROBIOLOGICAL PROPERTIES OF RANBIR SINGHPURA SOILS

Soil	PH	E.C., mmhos/cm.	O.C., %	Total N, %	Available Nutrients, mg./100 g.		Microbial Populations			
					N	P ₂ O ₅	Bacteria, 10 ⁶ /g	Actinomy- cetes, 10 ⁵ /g	Fungi, 10 ³ /g	Azoto- bacter, 10 ² /g
Narikhepar	6.3	0.34	0.48	0.04	17	2.2	17	17	24	2
Gegian	7.1	0.80	0.51	0.05	6	2.4	19	19	20	14
Kotli Shahdola	6.8	0.32	0.48	0.04	5	2.1	13	23	22	13
Kharian	7.8	0.57	0.22	0.02	17	2.3	18	25	14	14
Baggamarh	6.5	0.23	0.37	0.03	20	2.4	12	7	20	4
Makhanpur	7.0	0.23	0.54	0.06	18	2.4	16	19	18	2
Tinde	7.9	0.47	0.90	0.08	14	2.4	9	23	11	23
Miransahib	7.3	0.33	0.45	0.04	11	2.1	12	25	15	6
Purana Pind	8.3	2.00	0.75	0.07	14	2.3	10	21	12	2
R. S. Pura	7.2	0.73	0.62	0.06	14	2.3	21	24	15	6
Thikrian	6.1	0.20	0.45	0.05	20	2.5	14	18	27	6
Kotli	6.7	0.55	0.45	0.04	12	4.6	11	16	26	27
Barley	8.9	4.14	0.95	0.09	10	6.9	8	30	11	18
Bishnah	9.5	4.66	1.00	0.11	11	4.5	10	27	9	15
Darsopur	6.1	0.20	0.60	0.05	11	6.8	27	11	18	19
Mothey	8.6	3.66	0.85	0.07	14	4.6	13	24	13	21

E.C.—Electrical Conductivity; O.C.—Organic Carbon.

of organic matter which in turn gives low amount of these nutrients. The available nitrogen determined by alkaline permanganate method ranges from 5 to 20 mg./100 g., whereas available P₂O₅ was in the range of 2.1 to 6.9. According to the standards laid down for soil testing in India¹⁰, the amounts of available nitrogen and phosphate (P₂O₅) in these soils (112.5 to 450 kg. N and 47.5 to 155.0 kg. P₂O₅/ha. respectively) can be rated low to medium. This finding is consistent with earlier reports^{6,11}.

The bacterial population is in the range of 8 to 27 millions/g., which showed great variations in the distribution of this organism among these soils. Soil reaction may be the cause for these differences because bacteria are very sensitive to high alkalinity and acidity. This observation is in line with that of Alexander¹² but does not seem at par with that of Gupta⁶, who observed more bacterial count in acidic soils of Jammu and Kashmir. In his opinion⁶, the higher amount of organic carbon recorded in these soils can be the reason for bringing about more bacterial population as most of these soils come under temperate zone.

Actinomycetes was the next largest group of microflora after bacteria and lie between 0.7 and

3.0 millions/g. As expected alkaline and neutral soils are found to contain higher number of actinomycetes in contrast to acidic ones. This observation is in conformity with earlier reports of Mukherjee⁷ *et al*, Jha¹³ and Gupta⁶. Fungal count varies between 9 and 27 thousands/g., revealing the highest number of this organism in Thikarian and lowest in Bishnah. The lowest number in the latter case may be due to high pH because fungi are found to acid habitat. Large variations (200 to 2700/g.) in the distribution of *Azotobacter* in these soils may be ascribed to the variations of organic carbon, soil reaction and available phosphorus found in these soils.

All the soils contained, in general, more of Rod type bacteria than coccoid forms. Spore forming and Gram + were more than Gram—and non-spore formers. *Penicillium* followed by *Mucor* and *Rhizopus* were the dominant fungi in all the soils, except Narikhepar in which *Alternaria* was also observed. *Helminthosporium* and *Aspergillus* were often seen but in rare cases.

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Investigations were carried out with 3 levels of phosphorus, viz 0, 100 and 200 ppm, and 4 levels of sulphur, viz. 0, 50, 100 and 200 ppm, in a loamy sand soil using $\text{Ca}(\text{H}_2^{32}\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as a source of phosphorus and sulphur respectively, to study the effect of sulphur on the transformation of native and applied phosphorus under up-land conditions. The data showed that recovery of added phosphorus was in the order of saloid-P > Al-P > Fe-P > Ca-P at 0 days, and with time of incubation Ca-P and Fe-P increased while Al-P and saloid-P decreased. The application of sulphur increased the saloid-P and Al-P, while Ca-P and Fe-P decreased. Ca-P is not the dominant form in these soils to which added phosphorus is converted. Saloid-P remained high even after 42 days of incubation.

Effect of Sulphur on Transformation of Soil and Fertilizer Phosphorus

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Phosphorus fractionation studies have become vital for an elucidation of the nature of various compounds that may be formed in a soil on the addition of certain ions or phosphatic fertilizers. Saunder¹, and Khanna and Datta² reported that added phosphorus was fixed in aluminium compounds followed by iron compounds. Srivastava and Pathak³ observed that added phosphate in soil kept at field moisture capacity for 3 days almost completely recovered as saloid bound-P, Al-P, Fe-P and Ca-P. A good deal of information is, thus, available on the soil phosphorus fractions, but no literature is available on the effect of sulphur on the transformation of native and applied phosphorus (³²P).

The present investigation was, therefore, taken up to assess the effect of sulphur on the fate of native and applied phosphorus (³²P,) at 60 per cent of W.H.C. in a loamy sand soil.

Experimental

A loamy sand soil deficient in available phosphorus (5 ppm.) and sulphur (8 ppm.) was taken from Hissar for incubation studies. The experiment was conducted with 3 levels of phosphorus, viz. 0, 100 and 200 ppm, and 4 levels of sulphur, viz. 0, 50, 100 and 200 ppm, using $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as a source of phosphorus and sulphur respectively. The phosphorus was tagged at the rate of 0.25 mci/g. P_2O_5 . Thus, there were 12 treatments which were replicated thrice. 1 g. of soil was incubated in Corning glass tubes at 60 per

cent of water-holding capacity for 0, 7, 14, 28 and 42 days at $30 \pm 1^\circ\text{C}$ and after each period, one set of tubes was removed for fractionation studies. Inorganic phosphorus of the soil was fractionated according to the method of Chang and Jackson⁴ as modified by Fife⁵. Saloid-bound-P and Al-P in the extract were determined by the method of Dickman and Bray⁶, while Fe-P and Ca-P by that of Truog and Meyer⁷. The estimation of ³²P in different fractionates was carried out by G.M. Counter using side window tube.

Results and Discussion

The data (Table 1) reveal that the dominant forms of inorganic phosphorus in this soil were Ca-P (85 per cent) followed by Al-P and Fe-P (6 per cent), and saloid bound-P (3 per cent). Saloid bound-P decreased from 4.7 to 3.00 ppm, and Al-P from 14.0 to 13.0 ppm, whereas Fe-P increased from 15.0 to 20.0 and Ca-P from 200 to 207.5 ppm. in control with incubation upto 42 days. These findings are in agreement with those of Chaudhry⁸ and Gupta⁹. The recovery of the added phosphorus was in the order of saloid-P > Al-P > Fe-P > Ca-P at 0 days, and with incubation Ca-P and Fe-P increased at the expense of saloid bound and Al-P in control.

The increase in Al-P was due to the fact that aluminium-compounds are relatively more ionized than the corresponding iron compounds¹⁰, thus more of Al-P is formed from the added phosphorus and with

TABLE 1—TRANSFORMATION OF NATIVE AND APPLIED PHOSPHORUS (^{32}P) INTO VARIOUS FORMS OF PHOSPHORUS, PPM [AS AFFECTED WITH VARYING LEVELS OF SULPHUR AND TIME IN HISSAR LOAMY SANDY SOIL UNDER UPLAND CONDITIONS.]

Treat- ments	P_0				P_{100}				P_{200}			
	Saloid-P	Al-P	Fe-P	Ca-P	Saloid-P	Al-P	Fe-P	Ca-P	Saloid-P	Al-P	Fe-P	Ca-P
<i>0 days</i>												
S_0	4.7	14.0	15.0	200.0	58.7 (54.0)	48.0 (34.0)	26.0 (11.0)	200.3 (0.3)	124.7 (60.0)	76.0 (31.0)	31.0 (8.0)	204.0 (2.0)
S_{50}	6.0	16.0	15.0	197.0	62.0 (56.0)	42.0 (36.0)	23.0 (8.0)	197.2 (0.2)	128.0 (61.0)	79.0 (31.5)	30.6 (8.0)	199.0 (1.0)
S_{100}	6.2	17.0	14.5	196.0	64.5 (58.3)	33.2 (36.2)	22.5 (8.0)	196.2 (0.2)	129.2 (62.5)	79.0 (31.0)	30.5 (7.8)	197.2 (0.6)
S_{200}	6.2	17.0	14.3	196.0	65.4 (59.2)	53.2 (36.0)	21.3 (7.0)	196.2 (0.2)	128.8 (61.3)	79.6 (30.3)	30.3 (8.0)	197.0 (0.5)
<i>After 7 days</i>												
S_0	4.2	14.0	16.0	201.0	56.2 (52.0)	47.0 (33.0)	28.0 (12.0)	203.0 (2.0)	122.2 (59.0)	74.0 (30.0)	34.0 (9.0)	207.0 (3.0)
S_{50}	5.8	15.5	16.0	198.0	60.3 (55.0)	49.5 (34.0)	26.0 (10.0)	199.3 (1.3)	125.3 (60.0)	75.1 (29.8)	33.0 (8.5)	203.0 (2.5)
S_{100}	5.9	16.5	15.5	198.0	61.2 (55.2)	52.5 (36.0)	24.4 (8.9)	199.3 (1.3)	126.9 (60.5)	76.5 (30.0)	35.5 (9.5)	202.0 (2.0)
S_{200}	5.8	16.5	15.5	197.0	60.8 (55.0)	52.3 (35.8)	28.5 (8.0)	198.3 (1.3)	127.8 (61.0)	78.5 (31.0)	34.5 (9.5)	201.0 (2.0)
<i>After 14 days</i>												
S_0	4.0	13.5	17.0	203.0	47.0 (43.0)	46.0 (32.5)	33.0 (16.0)	208.0 (8.0)	116.0 (56.0)	69.5 (28.0)	39.6 (11.3)	210.5 (3.0)
S_{50}	5.2	14.3	16.5	198.0	51.2 (46.0)	47.8 (33.0)	30.5 (14.0)	204.0 (6.0)	122.2 (58.5)	72.3 (29.0)	36.9 (10.2)	204.0 (3.0)
S_{100}	5.5	15.7	16.0	197.0	52.8 (47.3)	49.7 (34.0)	29.0 (13.0)	202.0 (5.0)	123.1 (58.3)	76.1 (30.2)	37.0 (10.5)	202.4 (2.7)
S_{200}	5.5	15.0	16.0	197.0	53.0 (47.5)	50.5 (34.5)	29.0 (13.0)	202.0 (5.0)	123.1 (58.8)	76.6 (30.3)	37.3 (14.4)	202.0 (2.7)
<i>After 28 days</i>												
S_0	3.5	13.0	18.9	205.0	44.5 (41.0)	44.0 (31.0)	36.9 (18.0)	215.0 (10.0)	113.9 (55.2)	67.0 (27.0)	42.9 (12.0)	215.0 (5.0)
S_{50}	5.0	14.0	18.5	203.0	47.0 (42.0)	46.5 (32.5)	35.5 (17.0)	211.0 (8.0)	115.0 (55.0)	71.0 (28.5)	41.5 (11.5)	212.0 (4.5)
S_{100}	5.2	15.0	18.5	200.0	48.7 (43.5)	48.5 (33.5)	35.0 (16.5)	207.0 (7.4)	119.6 (57.2)	74.0 (29.5)	40.5 (11.0)	208.0 (4.0)
S_{200}	5.0	16.0	18.2	200.0	48.4 (43.4)	50.0 (34.0)	34.2 (16.0)	207.0 (7.0)	120.6 (57.3)	74.3 (29.4)	40.2 (11.0)	208.0 (4.0)
<i>After 42 days</i>												
S_0	3.0	13.0	20.0	207.0	43.0 (40.0)	44.0 (31.0)	39.0 (19.0)	217.0 (10.0)	111.0 (54.0)	65.0 (26.0)	44.0 (12.0)	225.0 (9.0)
S_{50}	4.5	14.0	19.5	204.0	44.5 (41.0)	46.2 (32.2)	38.0 (18.5)	212.0 (8.0)	112.0 (54.0)	70.0 (28.0)	42.5 (11.5)	220.0 (8.0)
S_{100}	5.0	14.3	19.3	200.0	47.4 (42.4)	47.8 (33.0)	37.3 (18.0)	207.0 (7.5)	115.0 (55.0)	73.3 (29.5)	42.1 (11.4)	213.0 (6.5)
S_{200}	5.0	16.0	19.0	200.0	47.2 (42.2)	59.5 (33.5)	37.0 (18.0)	207.0 (7.0)	115.0 (55.0)	76.0 (30.0)	41.4 (11.2)	213.0 (6.0)

(Figures in Parentheses indicate the per cent conversion of applied phosphorus)

prolonged incubation, Al-P is transformed to Fe-P¹¹. The application of 200 ppm sulphur increased the saloid bound-P and Al-P from 58.7 to 65.4 and 48.0 to 53.0 ppm, respectively, at 0 days of incubation. The Ca-P and Fe-P showed a decreasing trend with sulphur application and this was true both in case of native as well as fertilizer phosphorus. The same conclusion was drawn by Hernando *et al*¹², who reported that potassium sulphate had a depressive effect on the P-sodium hydroxide and P-sulphuric acid fractions. This could be due to the reason that addition of sulphur may bring about changes in the pH of medium and affect the phosphorus in soil solution, or the (SO₄)²⁻ ions may replace the phosphate ions in the exchange complex of soil. Secondly magnesium ions seem to depress the activity of calcium due to the addition of MgSO₄.H₂O which prevents the formation of Ca-P.

The data (Table 1) reveal that 34 and 31 per cent of 100 and 200 ppm phosphorus from monocalcium phosphate was immediately converted into Al-P in the absence of applied sulphur. However, 50 ppm sulphur in combination with 100 ppm phosphorus increased the Al-P to 36 per cent. The per cent Fe-P recovered decreased with sulphur application when incubated for 42 days. This may be attributed to the formation of iron sulphite and sulphate at the cost of breaking down of iron phosphate with sulphur application correspondingly increasing the phosphorus in soil solution, which combines with other forms of phosphorus. Similar conclusions have been drawn by Datta *et al*¹³ and Sperber¹⁴. The percentage recovered immediately as Ca-P was quite low being 0.3 and 2.0 per cent from 100 and 200 ppm phosphorus respectively, in the absence of sulphur. The per cent conversion of added phosphorus into Ca-P continued to increase with incubation period and it was highest after 42 days of incubation. The results show that in this soil, Ca-P is not the dominant form to which added phosphorus is converted since there was little increase in Ca-P with increase in time. Of course, the dominant form

of phosphorus in these soils is Ca-P, but initial compound formed are quite water-soluble and are extracted with ammonium chloride thus the immediate products of added phosphorus are in the order saloid-P > Al-P > Fe-P > Ca-P. However, with lapse of time Ca-P increases at the cost of saloid-P showing thereby that compounds of low solubility has started forming¹⁵. The saloid-P even after 42 days remained quite high. This form of phosphorus increased with sulphur application, but decreased with time.

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Seedlings of 3 Arhar cultivars, viz. T-17, S-8 and Prabhat were raised and maintained under identical field and soil conditions in the University botanical garden. One week old seedlings were inoculated separately with two different strains (mild and severe) of Arhar mosaic virus. The control plants being inoculated with distilled water simultaneously. The fungal population of the diseased and healthy plants were studied after 5 months of inoculation of post-flowering stage of the plants. The myco-organic make-ups of different cultivars differed appreciably in the quality as well as quantity which is evidenced by a much greater number of fungi/g. of dry soil at the root soil interface of healthy plants as compared to their diseased counterparts. The quality of fungi in diseased and healthy rhizosphere also showed marked difference. Appreciable effect of virus infection on rhizosphere was noticed. The diseased rhizosphere always exerted comparatively lesser effect. The minimum manifestation of rhizosphere effect was found with Arhar cultivar Prabhat infected with the severe strain of Arhar mosaic virus. The degree of reduction in the rhizosphere effect appeared to be dependent upon the degree of severity of virus infection, particularly in cultivar T-17.

Rhizosphere Mycofloras of Some Virus-infected Cultivars of Arhar [*Cajanus Cajan* L. Mill.]

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Bacteria and fungi find the root zone a more congenial environment wherein they congregate and multiply more rapidly than in the soil apart from the roots. However, comparatively little is known about the microflora of the root region of virus infected plants as compared to their healthy counterparts¹⁻⁴. Virus infected plants have been reported to be most commonly associated with physiological derangements, like decreased photosynthetic activity, increased rate of respiration, accumulation of soluble nitrogen compounds, increased activity of polyphenol oxidase and accumulation of oxidized polyphenol derivatives and altered activity of growth regulating substances⁶.

Such substantial derangements may induce considerable alterations in the microbial make-up of the plant rhizosphere. In this communication the authors have presented their observations on the non-rhizosphere and rhizosphere of three commercially important cultivars of Arhar infected with two different strains of Arhar mosaic virus in contrast with their healthy counterparts.

Materials and Method

Seeds of three Arhar cultivars (T-17, S-8 and Prabhat) obtained from U.P. Institute of Agricultural Science, Kanpur were sown separately in three different blocks

and seedlings raised under identical field and soil conditions. Each block containing the seedlings of a particular cultivar was further divided into three sections of 4 m. $\times$ 4 m. each. The distance between adjacent seedlings and rows was about one and three-fourth of a meter, respectively. Seven days old seedlings in the first and second sections in each block were inoculated with the severe and mild strains of Arhar Mosaic Virus (ASM and AMM) respectively, following Singh and Bhargava⁶. The seedlings of the third section served as control and were inoculated with sterile distilled water at the same time. The inocula of virus strains were initially isolated from field grown Arhar cultivar S-8 and maintained under glass house conditions on the same.

At post-flowering stage (after 5 months inoculation), the non-rhizosphere soil samples were taken from the fields of diseased as well as control sections, to a distance of about 40 cm. from the plants. The fungal population was assayed by soil dilution plate technique⁷ using modified Martin's medium⁸. The data about the number of colonies appearing on the nutrient plates were recorded and the percentage occurrence of the species calculated. The colony counts/g. of dry soil were determined by multiplying the average number of colony per plate by dilution factor with correction made for moisture content. Simultaneously, the rhizosphere

samples from the diseased and healthy plants were collected and fungal population determined following the procedure of Timonin⁹. The data obtained were used for the calculation of percentage occurrence and colony count/g. of dry rhizosphere soil as usual.

Results and Discussion

A perusal of data (Tables 1 and 2) reveals that the same number of fungal species (43) were encountered from the non-rhizosphere and rhizosphere of Arhar cultivars. Majority of the forms occurred in non-rhizosphere and rhizosphere soils both. Fungi like *Aspergillus clavatus*, *A. ustus*, *Chaetomium apiculatum*, *C. indicum*, *Helminthosporium rostratum*, *Papularia sphaerosperma*, *Penicillium spiculisporeum*, *P. stipitatum*, *P. variabile* and *Scopulariopsis chartarum* appeared to have established themselves in the non-rhizosphere soils only. *Absidia spinosa*, *Acremonium curtipes*, *Aspergillus awamori*, *A. tamaraii*, *Cephalosporium* sp., *Choanephora cucurbitarum*, *Cladosporium* sp., *Curvularia tuberculata*, *Myrothecium roridum* and *Phoma hybernica* were confined only to rhizosphere. Such differences in the species composition have already been examined by some workers^{10,11}. A closer examination of the data also reflects considerable variation in the species composition of different cultivars. *Absidia spinosa*, *Acremonium curtipes*, *Aspergillus flavipes*, *A. tamaraii*, *Curvularia geniculata*, *C. tuberculata*, *Scopulariopsis bravicaulis* and *Myrothecium convexum* were restricted to the rhizosphere of Arhar cultivar T-17 only. *Aspergillus fumigatus*, *A. glaucus* (gr.), *A. sydowi*, *Curvularia pallescens*, *Myrothecium roridum* and *Penicillium funiculosum* could be isolated only from the rhizosphere of cultivar S-8. Cultivar Prabhat, however, could show the restricted occurrence of only *Cladosporium herbarum*, *Sepedonium* sp. and *Syncephalastrum racemosum* in its rhizosphere. (Table 2). The non-rhizosphere soil was also different in this regard. *Alternaria tenuis*, *Chaetomium apiculatum*, *Curvularia geniculata*, *Helminthosporium tetramera*, *Mucor hiemalis*, *Papularia sphaerosperma*, *Penicillium spiculisporeum* and *Syncephalastrum racemosum* were confined to non-rhizosphere of T-17 only. *Aspergillus clavatus*, *A. fumigatus*, *Myrothecium convexum* and *Rhizopus nigricans* were present only in the non-rhizosphere of S-8. Non-rhizosphere of Prabhat, however, was least selective showing restricted occurrence of only *Chaetomium indicum* and *Cladosporium epiphyllum*. The quantity of fungi also varied in the root region of different varieties. These findings are in agreement with the observations of Obratzova¹² who noted that different kinds of rhizosphere exert different effects on its myco-organic component. He also found that a

variety which did not affect the number of micro-organisms in the root region did affect their qualitative composition. Thus, a specific plant itself appears as a decisive factor in establishing its specific fungal flora possibly because of specificity in chemical substances produced by the roots and sloughed off redundant tissues from the root system¹³.

While considering the rhizosphere fungi, it is evident that a total of 31, 30 and 18 fungal species were isolated from the rhizosphere (diseased and healthy) of Arhar cultivars T-17, S-8 and Prabhat, respectively. In all the cases, the majority of species were common to both diseased and healthy conditions. It is clear that there was no regular pattern as regards the number of fungal species in the diseased and healthy rhizosphere of different varieties. Mishra and Kamal¹⁴, while working with rhizosphere fungal flora of certain plants infected with viruses, reported higher number of species from diseased rhizospheres. Similarly, Kamal and Singh¹⁵ noted higher number of species in the rhizosphere of virus infected *Cynodon dactylon*. In the present investigation, however, only in case of cultivar T-17 such a possibility could be examined where 23 species were obtained from the rhizosphere of the plant infected with mild strain of Arhar mosaic virus as against 20 forms in its healthy counterpart. In rest of the cases either the number of species was almost the same in the rhizospheres of healthy and diseased plants or it was slightly lesser in diseased plants than that in the healthy ones. (Table 3). The rhizosphere of healthy plants exhibited higher colony count of fungi (per g. of soil) than those of diseased ones. This confirms the findings of the previous workers¹⁴⁻¹⁶. Recently, Gangawane¹⁷, while studying with the fungal flora of healthy and rosette virus infected groundnut rhizosphere, found that the virus altered the quantitative nature of the rhizosphere mycoflora so much so that only *Rhizoctonia solani*, *R. bataticola* and *Fusarium semitectum* could thrive in the rhizosphere of diseased plants as against several fungi in the rhizosphere of healthy plants. Such differences in the myco-organic make-ups can be connected with certain inherent differences in the physiological functioning of the diseased and healthy plants, making in the case of former, the conditions somewhat less favourable for general fungal development. It is known that in virus infected plants the carbohydrate content deviates substantially from the normal level and leads to an alteration in carbohydrate:nitrogen ratio¹⁷⁻²⁰. Such deviations in the metabolic set-up can account for quantitative and qualitative differences in the microbial population of their root region.

TABLE 1—PERCENTAGE OCCURRENCE OF FUNGI IN RHIZOSPHERE-FREE SOILS OF HEALTHY AND DISEASED ARHAR CULTIVARS

Organisms	Cultivars/Treatments								
	T-17			S-8			Prabhat		
	H	ASM	AMM	H	ASM	AMM	H	ASM	AMM
<i>Acrophialophora fusispora</i>	1.5	6.00	4.8	7.00	17.1	2.6	8.6	4.8	4.8
<i>Alternaria tenuis</i>	—	—	3.6	—	—	—	—	—	—
<i>Aspergillus aculeatus</i>	2.2	3.6	—	—	—	—	—	—	1.2
<i>A. clavatus</i>	—	—	—	—	—	13.2	—	—	—
<i>A. flavus</i>	0.7	—	36	—	—	32.3	4.0	—	9.0
<i>A. flavipes</i>	2.9	—	—	—	—	—	—	2.2	—
<i>A. fumigatus</i>	—	—	—	1.4	—	—	—	—	—
<i>A. glaucus</i> (g.)	—	—	—	2.4	2.9	0.6	4.0	2.4	2.4
<i>A. nidulans</i>	2.2	—	1.2	2.4	—	3.3	—	2.2	—
<i>A. niger</i>	15	3.6	—	5.6	3.8	—	2.0	—	1.2
<i>A. ochraceous</i>	—	—	—	—	2.9	0.7	—	—	2.4
<i>A. sydowi</i>	—	—	—	—	—	13.2	20.0	3.6	4.4
<i>A. terreus</i>	44.4	15.6	40.8	21.0	11.4	10.1	20.0	43.2	20.8
<i>A. ustus</i>	0.7	—	1.2	—	—	—	2.4	—	—
<i>A. versicolor</i>	—	—	—	—	2.9	—	—	2.2	1.8
<i>Chaetomium indicum</i>	—	—	—	—	—	—	—	2.4	—
<i>C. apiculatum</i>	—	1.2	—	—	—	—	—	—	—
<i>Cladosporium herbarum</i>	0.7	0.5	3.6	3.8	9.5	2.0	12.0	2.2	2.4
<i>C. epiphyllum</i>	—	—	—	—	—	—	—	—	1.2
<i>Curvularia geniculata</i>	—	—	6.0	—	—	—	—	—	—
<i>C. lunata</i>	5.3	1.2	—	3.8	—	2.0	—	—	—
<i>C. pallescens</i>	1.5	2.4	—	—	2.9	—	—	2.5	—
<i>Fusarium oxysporum</i>	27.5	21.0	19.2	4.2	3.8	19.1	4.0	9.6	4.8
<i>Helminthosporium tetramera</i>	—	2.4	—	—	—	—	—	—	—
<i>H. rostratum</i>	—	—	1.2	—	3.8	—	—	—	—
<i>Mucor hiemalis</i>	—	8.4	—	—	—	—	—	—	1.2
<i>Myrothecium convexum</i>	—	—	—	2.4	—	—	—	—	—
<i>Paecilomyces carioti</i>	—	—	1.2	2.4	—	—	—	—	—
<i>Papularia sphaerosperma</i>	—	—	1.2	—	—	—	—	—	—
<i>Penicillium funiculosum</i>	2.2	2.4	2.4	—	—	—	—	2.4	1.2
<i>P. luteum</i>	—	—	—	—	—	11.2	—	2.2	—
<i>P. Oxalicum</i>	—	—	—	—	—	—	—	1.2	1.2
<i>P. stipitatum</i>	—	4.8	—	—	3.9	—	2.0	—	—
<i>P. variable</i>	—	—	—	—	—	9.9	—	—	4.8
<i>P. spiculispurum</i>	2.3	—	—	—	—	—	—	—	—
<i>Rhizopus nigricans</i>	—	—	—	—	—	2.6	—	—	—
<i>Sepedonium</i> sp.	—	—	—	21.0	17.1	2.6	6.0	8.4	19.2
<i>Scolecobasidium constrictum</i>	—	—	—	—	—	—	—	1.2	2.4
<i>Scopulariopsis chartarum</i>	—	—	1.2	—	—	—	—	1.2	—
<i>S. brevicaulis</i>	—	—	1.2	19.6	—	—	10.0	—	—
<i>Syncephalasirum racemosum</i>	0.7	—	—	—	—	—	—	—	—
<i>Trichoderma viride</i>	3.7	—	—	3.4	—	1.3	2.0	1.2	1.2
Sterile colony	—	25.2	8.4	—	22.8	6.0	2.0	4.4	12.4

TABLE 2—PERCENTAGE OCCURRENCE OF FUNGI IN THE RHIZOSPHERE SOILS OF HEALTHY AND DISEASED ARHAR CULTIVARS

Organisms	Cultivars/Treatments								
	T-17			S-8			Prabhat		
	H	ASM	AMM	H	ASM	AMM	H	ASM	AMM
<i>Absidia spinosa</i>	—	—	1.4	—	—	—	—	—	—
<i>Acremonium curtipes</i>	—	—	2.8	—	—	—	—	—	—
<i>Acrophialophora fusicarpa</i>	1.5	—	—	0.7	—	—	—	—	—
<i>Aternaria tenuis</i>	0.4	—	—	1.4	—	—	—	—	—
<i>Aspergillus aculeatus</i>	1.9	3.6	—	0.7	0.5	1.8	3.8	2.4	1.2
<i>A. awamori</i>	—	—	—	0.7	—	—	2.1	2.4	2.0
<i>A. flavipes</i>	—	—	0.7	—	—	—	—	—	—
<i>A. flavus</i>	1.0	1.2	—	1.4	1.0	1.8	—	—	—
<i>A. fumigatus</i>	—	—	—	0.7	—	—	—	—	—
<i>A. glaucus</i> (gr.)	—	—	—	1.4	—	—	—	—	—
<i>A. nidulans</i>	—	2.4	—	2.1	1.5	3.6	3.2	2.4	2.1
<i>A. niger</i>	1.0	0.6	2.1	2.1	1.0	4.2	7.6	5.6	2.4
<i>A. ochraceous</i>	—	—	0.7	—	0.5	—	1.6	1.7	2.8
<i>A. sydowi</i>	—	—	—	0.7	—	0.6	—	—	—
<i>A. tamarii</i>	—	—	0.7	—	—	—	—	—	—
<i>A. terreus</i>	5.5	43.8	18.2	6.3	14.5	38.0	17.0	38.0	21.0
<i>A. versicolor</i>	2.0	—	1.4	—	—	—	—	—	—
<i>Cephalosporium</i> sp.	1.7	1.8	3.5	—	—	—	—	—	—
<i>Choanephora cucurbitarum</i>	0.5	0.6	1.4	—	1.0	0.6	2.0	2.4	1.0
<i>Cladosporium epiphyllum</i>	4.0	2.4	15.4	9.8	1.5	3.0	—	—	—
<i>C. herbarum</i>	2.2	1.8	2.8	3.5	4.0	2.8	1.5	2.4	1.2
<i>Cladosporium</i> sp.	—	—	—	—	—	—	1.3	2.4	2.5
<i>Curvularia geniculata</i>	—	—	2.8	—	—	—	—	—	—
<i>C. lunata</i>	2.1	3.0	1.4	4.2	2.0	4.2	1.3	4.2	2.2
<i>C. pallescens</i>	—	—	—	10.5	1.0	—	—	—	—
<i>C. tuberculata</i>	4.0	—	2.1	—	—	—	—	—	—
<i>Fusarium oxysporum</i>	60.0	24.6	22.4	21.1	46.0	32.4	3.8	8.4	1.8
<i>Hemionosporium tetramera</i>	—	1.8	1.4	3.5	—	—	—	—	—
<i>Mucor hiemalis</i>	4.0	2.4	2.8	2.0	4.8	2.4	49.4	2.8	1.8
<i>Myrothecium roridum</i>	—	—	—	0.7	5.0	—	—	—	—
<i>Myrothecium convexum</i>	2.5	—	—	—	—	—	—	—	—
<i>Paecilomyces varioti</i>	—	—	—	3.5	7.5	—	—	—	1.2
<i>Penicillium funiculosum</i>	—	—	—	—	1.0	—	—	—	—
<i>P. oxalicum</i>	—	—	4.9	4.9	—	—	—	—	—
<i>P. luteum</i>	—	7.0	8.4	0.7	—	—	1.2	2.4	1.2
<i>Phoma hybernica</i>	1.5	—	—	—	2.5	—	—	—	—
<i>Rhizopus nigricans</i>	2.0	1.8	1.4	0.7	0.5	1.2	—	—	—
<i>Sepedonium</i> sp.	—	—	—	—	—	—	3.6	2.8	57.6
<i>Sclebasidium constrictum</i>	1.0	—	—	—	3.0	—	—	—	—
<i>Scopulariopsis brevicaulis</i>	—	—	1.4	—	—	—	—	—	—
<i>Syncephalastrum racemosum</i>	—	—	—	—	—	—	0.2	2.8	0.1
<i>Trichoderma viride</i>	1.2	1.2	0.7	1.4	1.0	2.8	1.1	4.2	1.2
Sterile colony	—	—	—	16.9	—	—	—	12.6	—

TABLE 3—COLONY COUNTS/G. OF RHIZOSPHERE AND NON-RHIZOSPHERE SOILS AND R/S RATIOS IN DISEASED AND HEALTHY PLANTS OF DIFFERENT ARHAR CULTIVARS

Arhar Cultivars	Treatments/Factors			
	Treatments	Colony Counts/g Dry Rhizo- sphere Soils	Colony Counts/g Dry Rhizo- sphere-Free Soils	R/S Ratios
T-17	H	188030	100000	1.88/1
	AMM	78330	94000	1/1.20
	ASM	72910	89000	1/1.22
S-8	H	100580	89000	1.11/1
	AMM	81920	84000	1/1.02
	ASM	62679	75000	1/1.19
Prabhat	H	100340	85000	1.18/1
	AMM	86180	91000	1/1.05
	ASM	53200	81000	1/1.52

H = Healthy plants:

AMM = Plants infected with a mild strain of Arhar mosaic virus.

ASM = Plants infected with a severe strain of Arhar mosaic virus.

Differences in the rhizosphere mycoflora of diseased and healthy plants are again substantiated by the data obtained for the rhizosphere effects (Table 3). In all the three cultivars the R/S ratios are invariably higher in the healthy plants than their diseased counterparts. The maximum rhizosphere effect exercised by healthy plants of Cultivar T-17 followed by Prabhat and S-8. The minimum is exhibited by Prabhat infected by the severe strain of the virus. Such reductions in the rhizosphere effects can be connected with derangements in their physiological set-up manifested in the morphological abnormalities. The infection ultimately results in the reduced net assimilating area and relative growth leading to a reduction in carbon and nitrogen substrate. Thus the availability of root exudates is reduced, resulting in comparatively lesser congregation of fungi at the root soil interface of diseased plants. The degree of reduction in the rhizosphere effect appears to depend upon the degree of the severity of virus infection.

Conclusion

The rhizosphere mycopopulation of different Arhar cultivars differed considerably. The healthy and diseased plants of the same cultivar also showed a marked difference in myco-organic make-ups of their root region. The fungal flora of healthy plant-rhizosphere generally had an edge over that of the diseased one. In case of cultivar T-17, however, the rhizosphere of the

plant infected with the mild strain of the virus yielded higher number of species than that encountered from the corresponding healthy plant. The rhizosphere effect was always greater in the healthy plants than that of diseased counterparts. The minimum rhizosphere effect was manifested by cultivar Prabhat infected with the severe strain of the virus. The results readily fit in with the physiological derangements of the plants. The degree of quantitative reduction in the rhizosphere mycoflora of diseased plants appeared to be directly correlated with the degree of the severity of infection in case of cultivar T-17.

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The factors affecting the use of nitric acid for dissolution of beneficiated Egyptian rock phosphate of Sibaiya region has been investigated. From a study on the influence of these variables on the recovery of P_2O_5 , the following optimum conditions have been worked out : acid concentration 9 M : quantity of acid, 10 per cent in excess over the stoichiometric requirement ; period of acidulation, 30 min.; and temperature, $45^\circ \pm 0.1^\circ C$. The recovery is efficient even from rock samples of particle size 0.5 mm.; therefore, fine grinding of the rock prior to treatment with the acid is not considered necessary.

Nitrophosphates From Egyptian Rock Phosphate

Factors Affecting Dissolution of Sibaiya Rock in Nitric Acid

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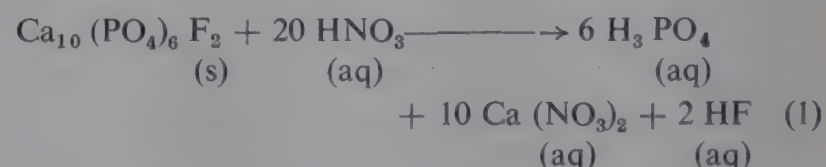
Normal superphosphate is manufactured locally by acidulating ground rock phosphate with sulphuric acid. Egypt possesses large deposits of rock phosphate but limited quantities of sulphur. As a result of the rapid world wide rise in the demand for sulphur and short supply in many areas, the delivery prices of sulphur for Egyptian fertilizer factories doubled about three times during the last 5 years¹.

It is therefore natural that Egyptian fertilizer manufacturers should take a close look at processes that require less or no sulphur, the most attractive of which is known as nitrophosphates or nitric phosphate, in which rock phosphate is treated with nitric acid. The cost of this acid is likely to fall because of the availability of natural gas in Egypt and the technological improvements in converting ammonia to nitric acid. Moreover, the nitrate ion supplies nutrient nitrogen and ends up in a product, either with the phosphate or in a coproduct nitrogen fertilizer, whereas in sulphuric acid treatments, the sulphate ion serves no useful purpose and the gypsum formed having very low nutrient value dilute the product.

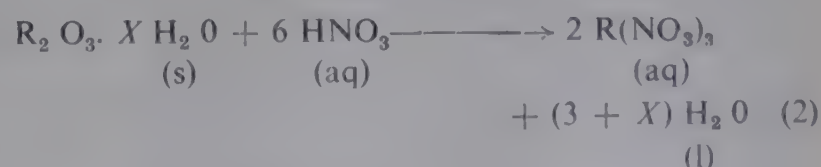
Early researchers recognized that the hydrogen ion in the acid is the important factor in acidulating rock phosphate. In processes developed in Europe²⁻⁶ and the USA⁷⁻¹², the rock phosphate is acidulated with nitric acid or a mixture of nitric acid with sulphuric or

phosphoric acid and the slurry is ammoniated, dried and granulated.

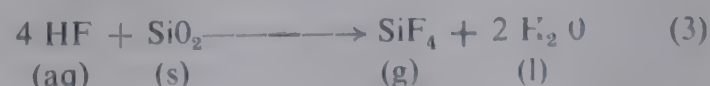
The factors affecting the dissolution of rock phosphate in nitric acid include fineness of grain, period of acidulation, acid concentration, temperature, and acid-to-rock ratio. The treatment of rock phosphate with nitric acid can be approximately described in terms of a principal conversion reaction and several side reactions. Fluorapatite being the major constituent of phosphate rock, the principal reaction is¹³.

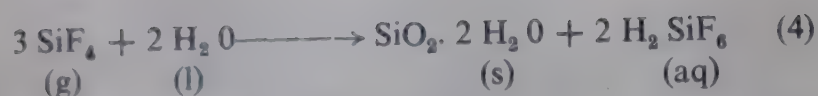


The side reactions are caused by the reaction of impurities present along with apatite with nitric acid. The important ones are



(where R may be iron or aluminium)





The estimation of nitric acid requirement for the dissolution of rock phosphate has been made on the basis of a correct analysis of the sample used, so that the stoichiometrics of the main and the side reactions can be taken into account¹⁴⁻¹⁶.

The present communication presents the results of a study on the factors affecting the dissolution of an Egyptian rock phosphate sample of Sibaiya region with nitric acid.

Experimental

Materials : The main materials used were the beneficiated Egyptian phosphate ore of Sibaiya and locally produced nitric acid. Chemical analysis of the ground rock was carried out before and after beneficiation according to the standard methods¹⁶⁻¹⁸. The original phosphate ore analysed as follows¹⁹ : P_2O_5 , 21.2 ; CaO , 45.2 ; MgO , 0.2 ; R_2O_3 , 3.6 ; SO_3 , 1.2 ; F , 3.3 ; CO_2 , 15.1 ; and SiO_2 + acid insoluble, 10.2 per cent. This material was beneficiated in the laboratory before treatment with nitric acid by calcining at 950°C for 2 hours to decompose calcium carbonate present, quenching in distilled water, and extracting the lime by counter-current washing using a simple cell similar to that described by Bardhan *et al*²⁰. A typical beneficiated sample analysed as follows : P_2O_5 , 32.5 ; CaO , 43.7 ; R_2O_3 , 4.4 ; SO_3 , 1.3 ; F , 4.2, CO_2 , 0.9 ; and SiO_2 + acid insoluble, 12.8 per cent.

Influence of Variables on the Efficiency of Dissolution of P_2O_5 : The following sized fractions (mesh BSS) of beneficiated ground rock particles were used : $-36 + 85$, $-85 + 120$, $-120 + 170$, and -170 . A weighed sample of each fraction was added to the stoichiometric requirement of 9 M nitric acid, kept at a constant temperature ($45^\circ \pm 0.1^\circ\text{C}$) using a thermostatic water bath. The period of contact in each case was varied from 5 to 120 min. and the mixture of rock and acid was kept constantly stirred using a constant speed (1200 rpm) mechanically agitated stirrer. At the end of a specified time interval, the slurry was filtered and the filtrate analysed for P_2O_5 .

Another series of experiments was conducted to find out the influence of acid concentration and temperature on the efficiency of extraction of P_2O_5 . For this purpose, different lots of sample, so ground that 98 per cent passed through 36 mesh (BSS), were treated with nitric acid of concentration varying from 6 to 12 M and at temperature varying in the range $25-55^\circ\text{C}$. The period

of contact between rock phosphate and acid was varied in each case from 15 to 90 min.

The object of another series of experiments was to determine the optimum acid-to-rock ratio for getting the maximum recovery of P_2O_5 . Using sample so ground that 98 per cent passed through 36 mesh (BSS), the above ratio was varied from 20 : 1 to 30 : 1, keeping the temperature and period of contact constant at $45^\circ \pm 0.1^\circ\text{C}$ and 30 min. respectively.

Results and Discussion

The results are given in Figs. 1-6.

Influence of Particle Size : It is obvious that rock dissolution is equally efficient at all particle size tried, and that the reaction of the rock with nitric acid proceeds almost equally as rapidly with large particle size fractions as with finely ground material (Fig. 1).

Influence of Period of Acidulation : The data presented in Fig. 1 show that the major part of P_2O_5 is extracted within the first 10 min. A reaction time from about 10 min. to about 1 hr. is sufficient to almost completely dissolve the P_2O_5 present. However, for practical considerations, 30 min. may be taken as the optimum period.

Influence of Acid concentration and Temperature : The data presented in Figs. 2-5 indicate that the recovery of P_2O_5 falls with increase in acid concentration ; satisfactory results are obtained by using 6-10 M acid. The concentrations of nitric acid below 6 M are not desired to avoid excessive dilution of the resulting slurry. The reduced recovery of P_2O_5 with high acid concentration is possibly due to precipitation of complex calcium nitrophosphates.

From the general nature of the curves (Figs. 2-5), it is evident that the dissolution of rock phosphate increases with increase in temperature from 25 to 55°C . The effect of temperature on the P_2O_5 recovery varies with acid concentration and decreases with increasing period of contact between rock and acid. The interaction between the effects of acid concentration and temperature on the recovery of P_2O_5 suggests the adoption of 9 M and $45^\circ \pm 0.1^\circ\text{C}$ as the optimum acid concentration and temperature respectively.

Influence of Acid-to-Rock Ratio : The data presented in Fig. 6 shows that though there is a slight increase in the recovery of P_2O_5 on the acid-to-rock mole ratio beyond 20 : 1, the advantage being more than offset by a much higher cost of nitric acid. Therefore, unless excess nitric acid is required for further processing of the

resulting slurry into nitrophosphate fertilizers, the acid-to-rock mole ratio should not be more than 22 :1 or corresponding to 10 per cent in excess over the stoichiometric requirement as per reaction 1.

The optimum conditions of the results of the present study indicate that fine grinding of phosphate rock is

not necessary for attaining satisfactory recovery of P_2O_5 . A material as coarse as 0.5 mm. is attacked by nitric acid rapidly. The optimum conditions for dissolution are : acid conc., 9 M ; quantity of acid, 10 per cent in excess over the stoichiometric requirement ; period of acidulation, 30 min.; and temperature, $45^{\circ} \pm 0.1^{\circ}C$.

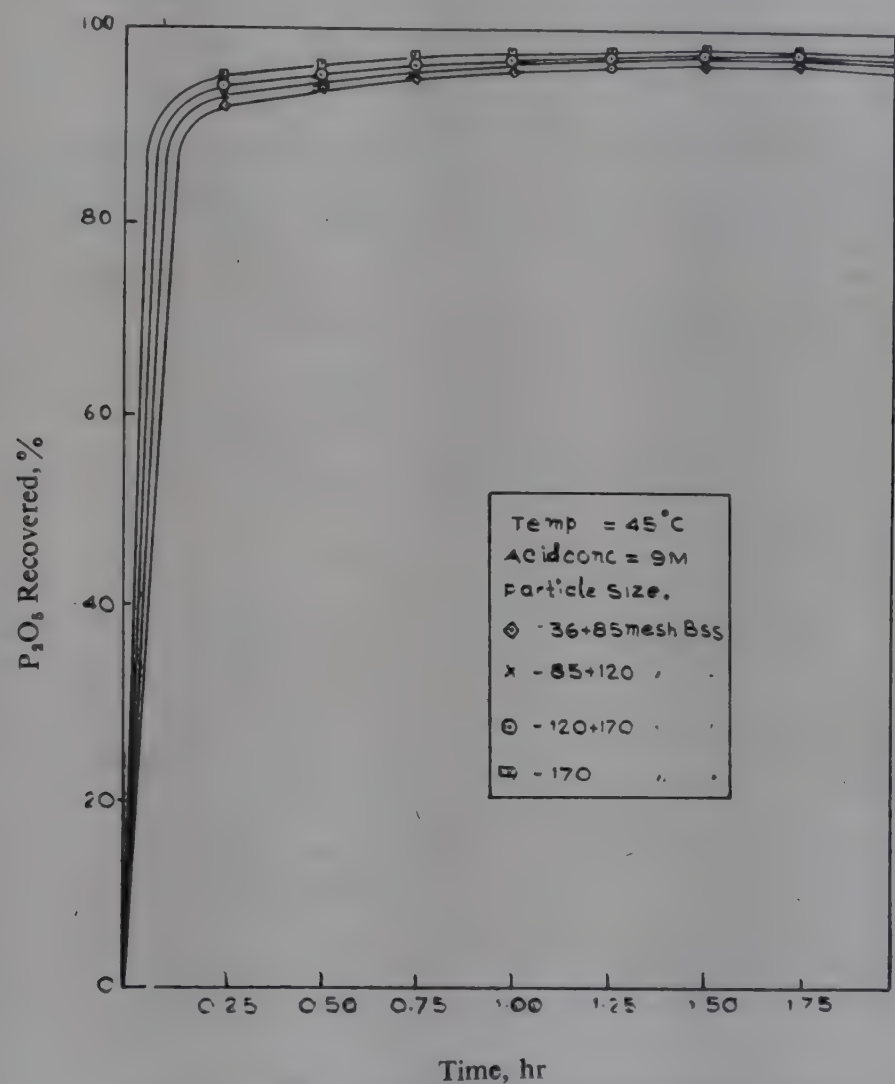


Fig. 1—Influence of Particle Size on the Recovery of P_2O_5

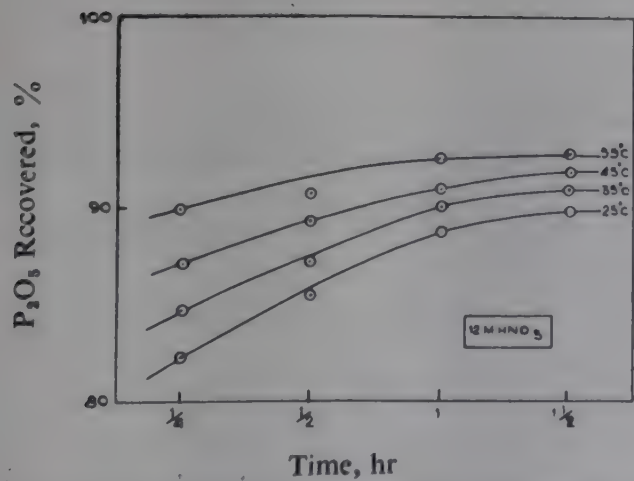


Fig. 2—Influence of Temperature on the Recovery of P_2O_5 at 12M Nitric Acid.

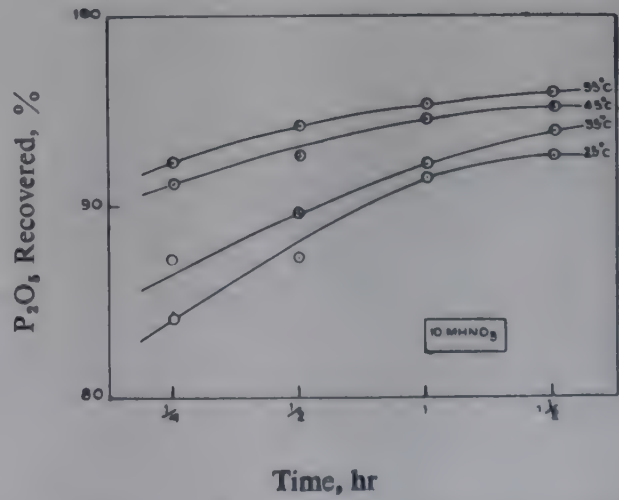


Fig. 3—Influence of Temperature on the Recovery of P_2O_5 at 10M Nitric Acid.

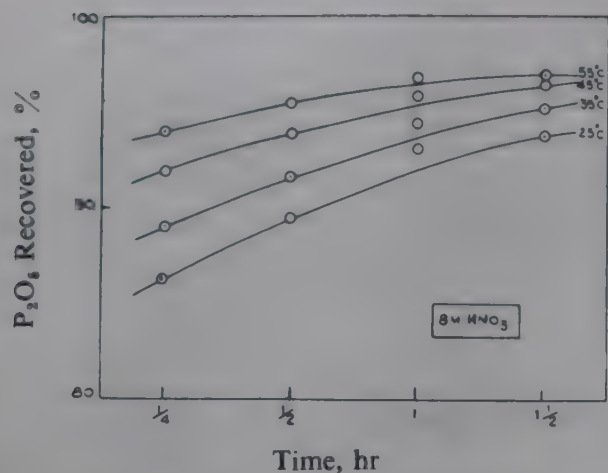


Fig. 4—Influence of Temperature on the Recovery of P_2O_5 at 8M Nitric Acid.

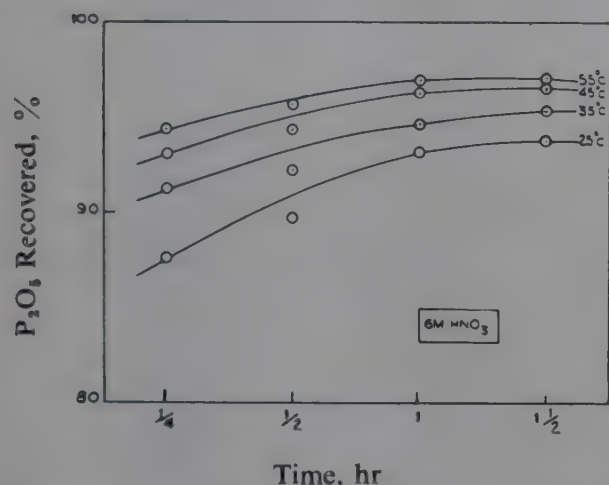


Fig. 5—Influence of Temperature on the Recovery of P_2O_5 at 6M Nitric Acid.

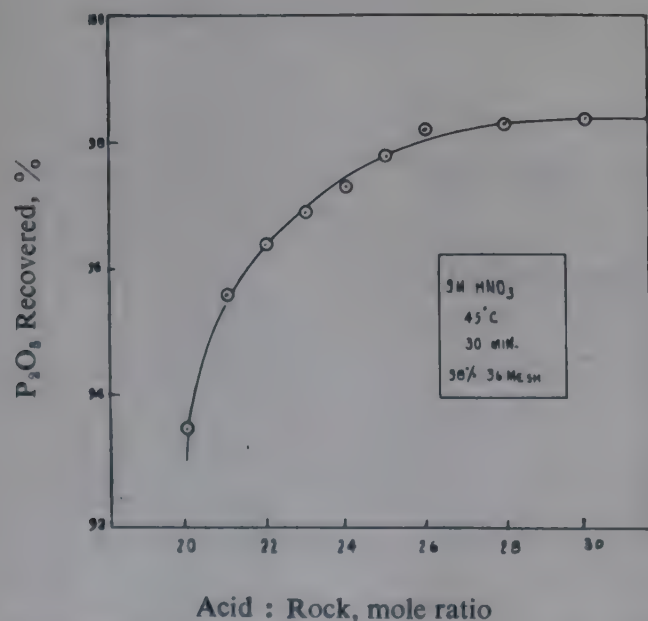


Fig. 6—Influence of Acid : Rock mole Ratio on the Recovery of P_2O_5 .

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Silica gel, prepared by varying the pH (between 1.5 and 6.0) and the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio (0.35 to 0.79), shows that increase in the pH value decreases the setting time, whereas the increase in the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio increases the same. The surface area of the dried gel decreases with the increase of pH, while the average grain diam., pore volume and average pore diam. increase with pH. Whereas the silica gel prepared by the increase of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio, the surface area, total pore volume, average grain diam. and average pore diam. increase up to the ratio 0.54 and with further increase in the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio, surface area, total pore volume, average pore and grain diam. decreases. The pore size distribution measurement shows that 88-90 per cent (in case of pH variation) and 90-91 per cent (in case of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio variation) pores are in the region of 4-60 Å.

Effect of Variation of pH of Gelation and Soda : Silica Ratio on the Characteristics of Silica Gel

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Introduction

The method of preparation of a solid catalyst bears a relationship with the activity, selectivity and life of the catalyst.

Silica gel, as an industrial catalyst and catalyst support, finds application in reactions, such as hydrogenation of benzoic acid, aniline, fatty acids and their derivatives, etc., for the reformation of methane, propane, butane, natural gas, liquified petroleum gas and light distillate, and in the dealkylation of toluene. It is also used as a catalyst for alkylation, detritylation of carbohydrates, oxidation of nitrous oxide to nitric oxide and cracking of cumene and similar reactions.

Silica gel can be prepared by adding acid to a fairly concentrated solution of sodium metasilicate or water glass. Various authors¹⁻⁶ have studied the conditions for gelation, effect of aging in various media and its effect on the nature of silica gel. In general, the setting time of the mixture of sodium silicate and acid, without the addition of foreign agents, depends upon the concentration, pH of the mixture and the temperature of setting⁷. Neutral or slightly acidic mixture sets to a gel most rapidly⁸. With pH between 4.4 and 6.0 for acetic acid and between 4.2 and 5.5 for hydrochloric acid, the rate of gelation is a linear function of hydrogen ion concentration⁹⁻¹². Sing and Madeley¹⁴ studied the effect of pH on the setting time and measured the

nitrogen adsorption and desorption isotherms of the dried gels and compared the surface area obtained from above and nitrous oxide adsorption. Mitchell¹⁵ studied the effect of pH on the surface area and the reactions involved in the adsorption of water vapour and other organic vapours on the surface of the silica gel.

In the present investigation, the authors have studied the effect of variation of pH in the range 1.5-6.0 and that of soda: silica ratio between 0.35 and 0.79 on the setting time and the textural properties of the dried gels. The temperature and the concentration of acid and silicate were maintained same throughout. The studies may provide guidelines for the tailormade catalyst and support preparation.

Experimental

A. Preparation of the Samples: Commercial grade sodium silicate having the following analysis, was used for preparation of the gels: sodium silicate 36-37 per cent, silica 27.2 per cent, sodium oxide 10.2 per cent ferric oxide 0.06 per cent based on silica, and sp.gr 1.4.

Variation of pH: Diluted sodium silicate (sp.gr. 1.17) was slowly added to the 10 per cent hydrochloric acid solution with vigorous agitation, till the desired pH was obtained¹⁶. The mixture was allowed to set at room temperature and the setting time was recorded in the Ostwald viscometer. The resulting gel was washed with distilled water (pH 6.8) till free from chloride

ions and dried in the air oven at 110°C for 72 hours. The samples were sized by sieving to 16-20 mesh (BSS) sieves for the textural studies.

Variation of Soda/Silica Ratios: In this case the gel was prepared by the same method as above except that the variation of soda: silica ratio was achieved by adding a weighed amount of solid caustic soda to a sodium silicate solution of 1.17 specific gravity. For all the ratios, the final pH of the mixture was 3.0. The samples were dried after washing for 72 hours and sized to 16-20 mesh.

B. Measurement

(i) **Soda and Silica:** Soda and silica contents in the original solution were estimated by the standard methods.

(ii) **Surface Area:** Surface area was measured by BET method.

(iii) **Setting Time:** The setting time of the gel was recorded by Ostwald viscometer during the determination of change in flow time with the aging and the setting time was considered when there was no movement of fluid in the viscometer.

(iv) **Pore Size Distribution:** The total pore volume was determined by mercury and helium displacement, and the pore size distribution was determined by the Aminco Winslow porosimeter having working range upto 15,000 psi.

Results and Discussion

Silica gel is a macromolecular gel which is formed from sodium silicate upon acidification. According to Willstatter *et al*¹⁷, mono- or disilicic acids are formed in the reaction, which undergo polymerization, giving

rise to a high molecular silicic acid. Since polymerization is a three dimensional process, a molecular network is built of —Si—O—Si— units. Initially this network results in very small highly hydrated particles with little inter-particle bonding. Only at a later stage just before the hydrogel formation, the inter-particle bonds become important and lead to gelation. The condensation reaction continues after the hydrogel has formed and eventually leads to syneresis²⁸.

Hurd *et al*^{18,19} showed that the silica gel formation is not due to the coagulation of silicic acid solution. Considering the process of silica gel formation according to the laws of the velocity of ordinary chemical reaction, Hurd *et al*^{18,19} obtained an activation energy value of 16,640 calories which is analogous to Arrhenius heat of activation for a homogeneous chemical change.

It is assumed that the polymerization takes place in three steps, viz. (1) the first step in which the monomer molecule is activated to form a radical, (2) the chain growth, in which the great number of activated monomer radicals are attached to each other forming the polymer chain which is, however, still a radical (macroradical) (3) the final reaction, by which the macro radical is converted to macromolecule losing its reactive power. The macromolecules condense to form a gel.

The plots of pH vs log t and $\text{Na}_2\text{O}/\text{SiO}_2$ vs log t, where t is the setting time, indicate the presence of more than one kinetic stage in the gelation of sodium silicate and acid mixture and each stage is characterized by its own parameters (Figs 1-2). The three breaks observed may be inferred as the three stages of polymerization reaction.

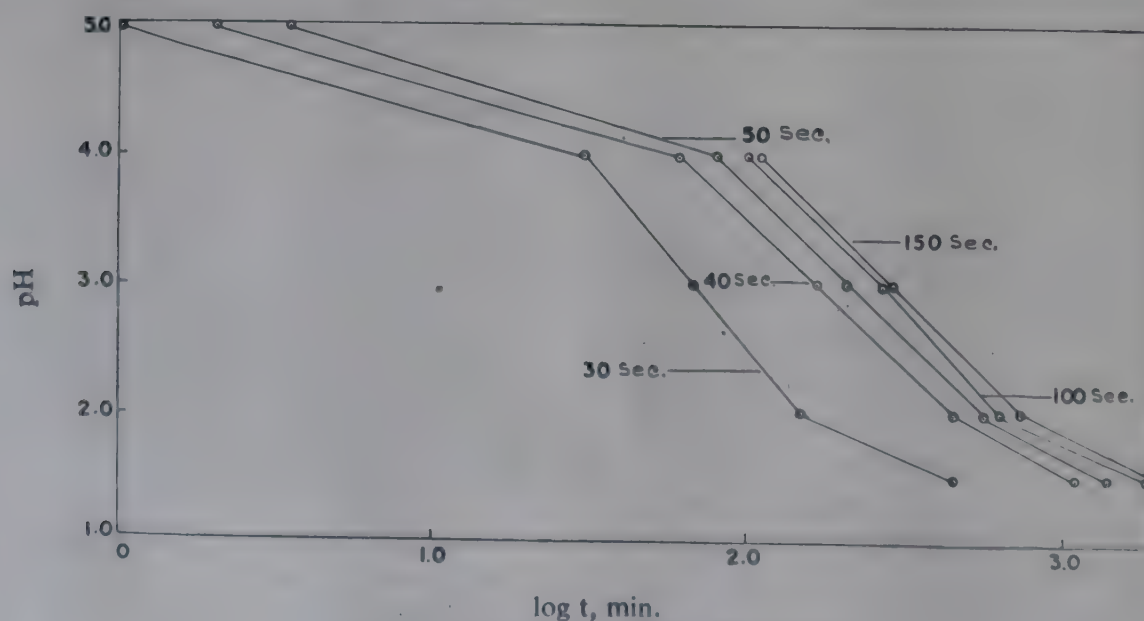


Fig. 1—Plot of pH vs Ageing Time (log t)

Effect of pH Variation: The setting time of the sodium silicate and acid mixture decreases as the pH value increases from 1.5 to 6.0. At pH 1.5, the setting time is 19.8×10^3 min. and as the pH reaches 6.0 the setting takes place almost instantaneously (Fig. 3). This shows that hydrogen ion concentration has a catalytic effect on the setting of silica gel.

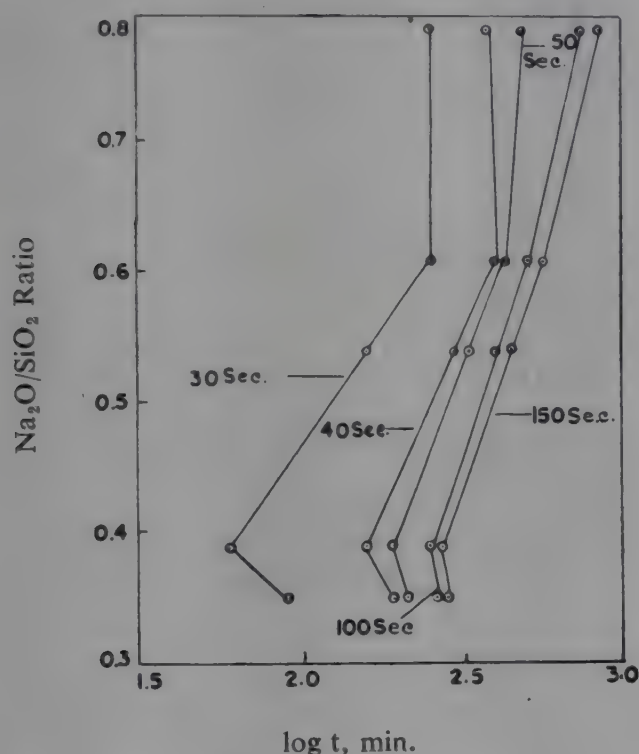


Fig. 2—Plot of Na₂O/SiO₂ Ratio vs Ageing Time (log t).

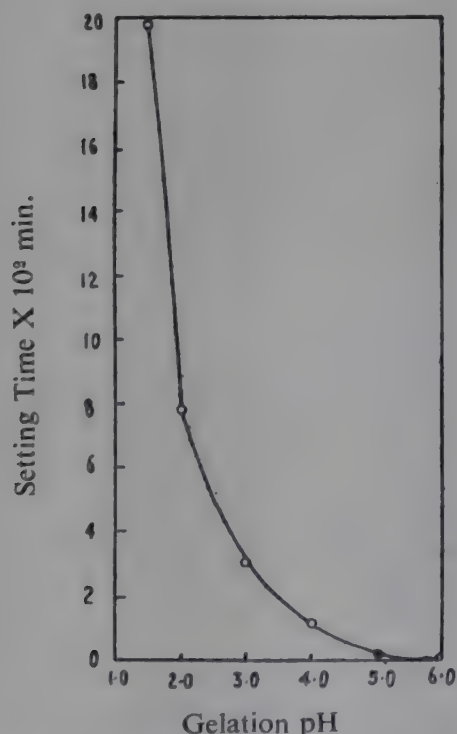


Fig. 3—Effect of pH on the Setting Time.

On drying these gels after the removal of electrolyte at 110°C for 72 hours, it may be seen (Fig. 4), that the surface area is decreasing with increasing the pH value of gelation while the total pore volume is in-

creasing. Numerous workers^{14,20-23} have studied the effect of pH on the surface area which is determined by the size of the elementary particle. Larger surface results at the pH where the condensation is minimum and the elementary particles are small. This seems to occur at lower pH values. At higher pH, the rate of condensation is such that the larger elementary particles are formed. From the aggregation of small particles, a higher surface area gel will result with lower pore volume, whereas from the aggregation of the larger elementary particles the surface area of the gel will decrease and the total pore volume will increase. The results in Fig. 4 in fact show that at pH 1.5 the surface area is higher (709 m²/g.) and as the value is increasing to pH 6.0, the surface area decreases to 388 m²/g., whereas the total pore volume increases from 0.22 to 0.69 cc./g. The average grain diameter at pH 1.5 is 58.1 Å which increases to 176.9 Å at pH 6.0, and the average pore diameter also increases from 12.6 to 71.6 Å with the increase of pH value (Fig. 5). It may be seen from the pore size distribution measurement (Table 1) that 88-90 per cent pores fall in the region 4-60 Å, when the pH of the mixture of sodium silicate and acid increases from 1.5 to 6.0. The pH

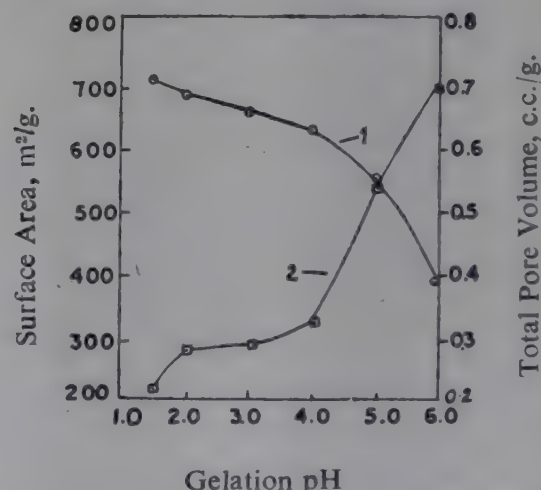


Fig. 4—Effect of pH on the Surface Area and Total Pore Volume

- Legend
1. Surface Area
2. Total Pore Volume.

of gelation is thus found to have a profound effect on the properties of the dried gels. The dried gel obtained at lower pH is formed from the condensation of smaller macromolecules during gelation. This results in finer particles, having smaller grain and pore diameter and lower pore volume in the dried gel. The surface area is, however, maximum in this sample because it (m²/g.) is normally more in case of finer particles. At higher pH, the condensation during gelation is pronounced, resulting in the formation of larger macro-molecules which in the dried gel results in comparatively larger grain

diameter, pore diameter and pore volume. But the surface area of the gel formed at higher pH is lower, because of the larger particles. The pH of gelation,

therefore, controls the size of the macro-molecules during gelation on which finally depends the textural properties of the dried gel.

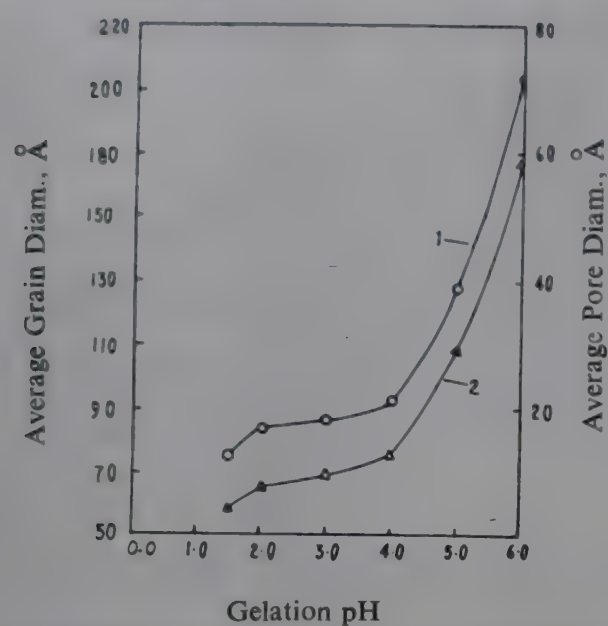


Fig. 5—Variation in Average Pore and Grain Diameter with Increase in pH of Gelation

1. Average Pore Diam., Å; 2. Average Grain Diam., Å

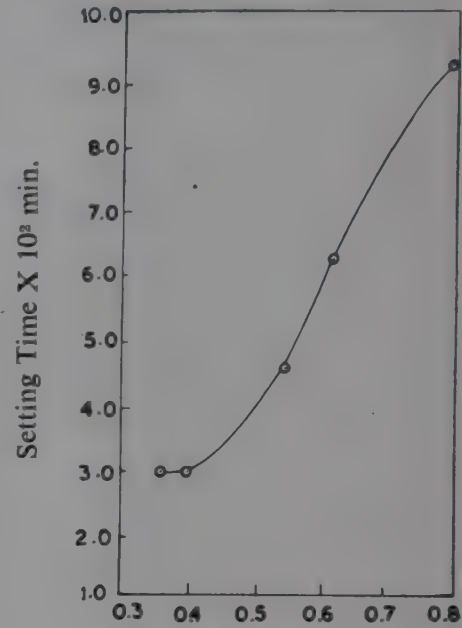


Fig. 6—Variation in the Setting Time of Silica Gel with Na₂O/SiO₂ Ratio.

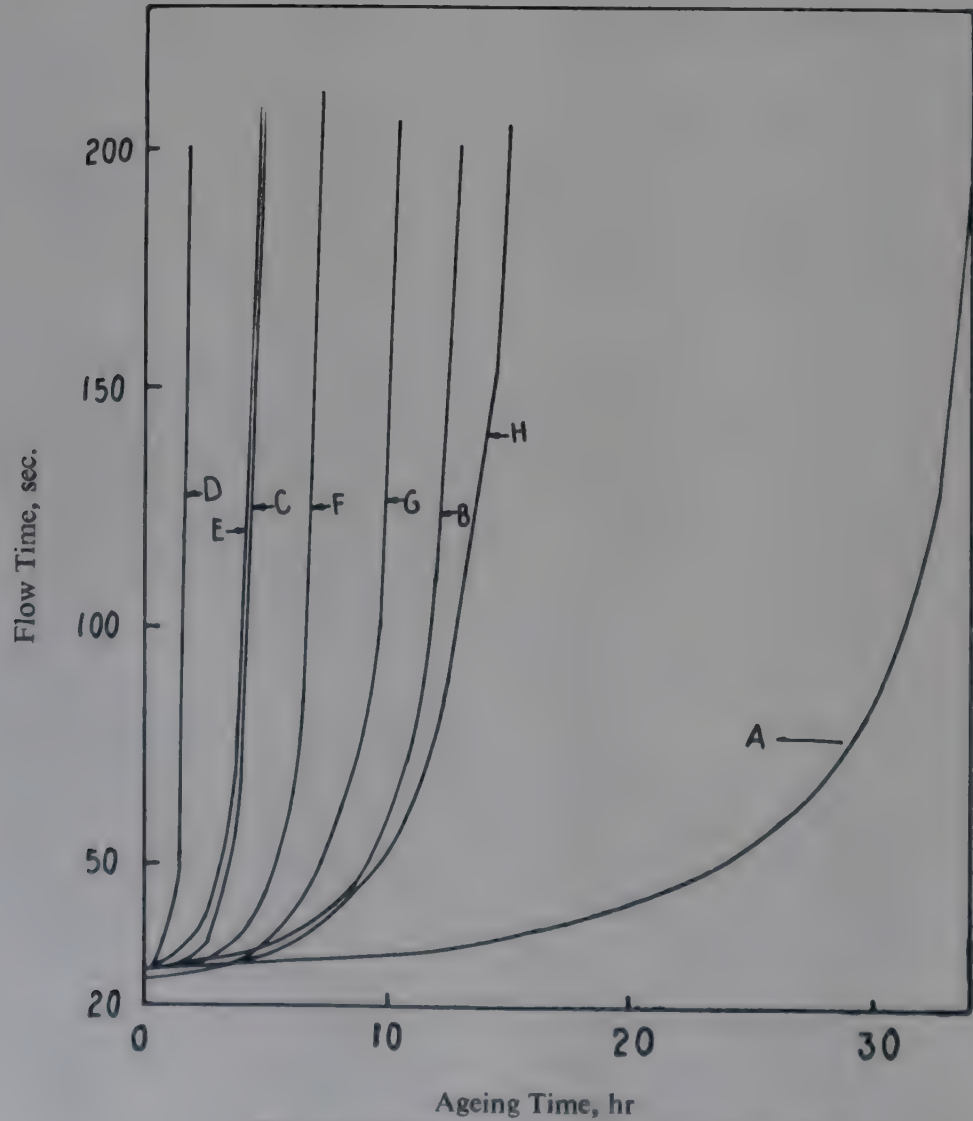


Fig. 7—Relation between Ageing and Flow Time

Effect of Soda/Silica Ratio : In this case also, the setting time of the mixture of sodium silicate and acid while maintaining the same pH increases with the increase of soda: silica ratio. When the ratio is 0.35 the setting time is 3×10^2 min. which remains same upto a ratio of 0.39 and then increases to 9.3×10^2 min. at a ratio of 0.79; as shown in Fig. 6. This may be due to the concentration of silica present in the system, and as the amount of silica is decreasing with the increasing ratio of soda: silica, the sodium in the system is playing a predominant role in the process of setting. According to Moulik and *et al*²⁴ the gelation of silica gel depends upon the concentration of silica present in the system.

It, therefore, appears that up to a certain range, the soda: silica ratio is not an important factor in the polymerization process (from 0.35 to 0.39); on further increase of sodium beyond this range, it retards the process of the polymerization of silicic acid thus increasing the setting time. This can also be seen (Fig. 7) from the decrease flow time with reference to any point on the ageing as sodium content of the system is increasing. It may thus be concluded that both pH and sodium concentration affect the polymerization process but with opposite effect.

Upon the removal of electrolytes by washing the resulting gel and drying it at 110°C show an increase of its surface area from 658.1 at soda: silica ratio 0.35 to 707.8 m²/g. at 0.54 and then decreasing gradually to 662 m²/g. When the ratio increase to 0.79 (Fig. 8). the total pore volume, average grain diam., and average pore also follow the same pattern as indicated in Figs 8 and 9. The pore size measurements (Table 1) show that the 90.1-91.1 per cent pores are lying in the range of 4-60 Å and their average pore diameter varies from 19.5 to 15.9 Å units. It may be concluded that upto the soda: silica ratio 0.54, the sodium present in the system may be exposing the pores of silica gel which are contributing to the high silica gel surface, while the further increase in the soda: silica ratio decreases the

surface area by dissolving the silica from the very finer pores and depositing it on the wider pores and also blocking some of the pores, thus rendering in the decrease of the total pore volume and surface area. This process may be more and more predominant as the sodium content of the system is increasing.

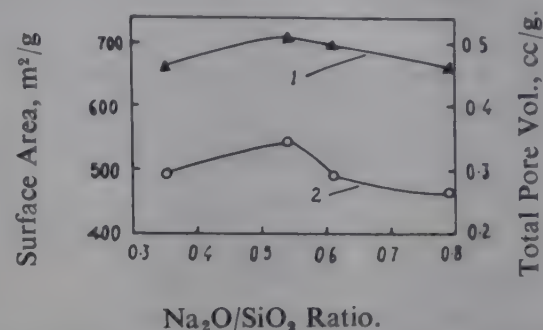


Fig. 1—Effect of Na₂O/SiO₂ Ratio on the Surface Area and Total Pore Value

1. Surface Area 2. Total Pore Volumic

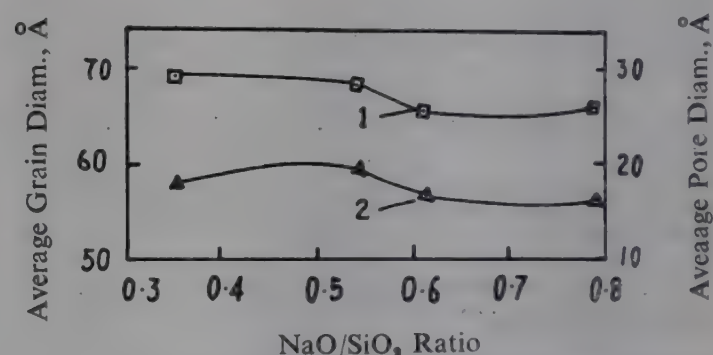


Fig 9—Effect of Na₂O/SiO₂ Ratio on the Average Pore and Grain Diameter

1. Average Grain Diameter 2. Average Pore Diameter

Conclusion

The surface area decreases with the increase of pH value, whereas the total pore volume, average grain size and average pore diameter increases with the increase of pH value. The variation of soda: silica ratio shows that the surface area, total pore volume, average grain size and average pore diameter increases up to the soda/silica ratio of 0.54 and then decreases with further increase of soda: silica ratio.

TABLE 1—PORE SIZE MEASUREMENTS OF SILICA GEL

Pore Size, Å	Pore Size Distribution at Different pH					Pore Size Distributon at Different Na ₂ O/SiO ₂ Ratio				
	1.5	2.0	3.0	4.0	5.0	6.0	0.35	0.54	0.61	0.79
4- 60	86.7	88.1	90.1	90.2	88.7	88.8	90.1	91.2	91.1	91.9
60- 100	5.3	4.8	3.4	3.7	3.7	4.3	3.4	2.8	3.3	2.9
100- 175	2.6	2.2	2.1	2.6	2.2	2.6	2.1	1.9	1.8	1.8
175- 300	1.2	1.0	1.3	0.9	1.3	1.2	1.3	1.2	1.0	0.9
300- 400	0.6	0.4	0.2	—	0.4	0.6	0.2	0.1	0.4	0.25
400- 500	0.5	—	0.1	0.2	0.2	0.3	0.1	0.1	0.2	0.38
500-7500	2.8	3.1	2.6	2.1	2.6	1.7	2.6	2.4	1.6	1.75

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The reduction kinetics and mechanism of a nickel oxide catalyst finely dispersed on a matrix, comprising 40 per cent alpha and 60 per cent gamma aluminas, have been investigated. The temperature programmed reduction data obey the first order rate equation of Coats and Redfern giving an apparent activation energy of 35.1 K cal/mole. Auto-catalysis was not observed upto 16 per cent reduction of the oxide. The mechanism of reduction has been attributed mainly to the reaction of gaseous molecular hydrogen with the nickel oxide surface.

Evaluation of the Reduction Kinetics and Mechanism of Supported Nickel Oxide from Thermogravimetric data

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Introduction

Reduction of the unsupported nickel oxide was found to be an auto-catalytic process by Benton and Emmett¹, in which the rate is governed by the catalysed action of the reduced nickel particles present at the nickel-nickel oxide interface. Later, Bandrowski *et al*² observed that the overall rate of reduction is given by the sum of two rates firstly, a slow process arising from the reaction of the molecular hydrogen with the metal oxide and secondly, a much faster rate contributed by the atomic hydrogen dissociatively absorbed at the nickel-nickel oxide interface. The present authors³, however, observed that the reduction mechanism is not necessarily the same for the supported nickel catalysts having finely dispersed active component uniformly distributed over the carrier surface. This is so because the individual nickel oxide particles are separated from each other by high energy barriers of the bare surface of the support material, and hence nickel-catalysed reduction is not favoured. In this communication, the kinetics of reduction for a finely dispersed nickel catalyst have been presented using the first order decomposition equation of Coats and Redfern⁴.

Experimental

Preparation of the Sample: The finely powdered α alumina precalcined at 1300° C, was suspended in an aqueous solution of nickel and aluminium nitrates and heated to boiling, then precipitated with Carb-

liquor (carbon dioxide saturated in ammonia solution) with constant stirring. The precipitate was thoroughly washed, dried and then cured in air at 600°C for 6 hr. in a muffle furnace. Chemical analysis showed that the finished catalyst contained 8 per cent nickel in a composite matrix of α and γ aluminas.

Temperature Programmed Reduction: A dry and weighed amount of the finely powdered catalyst was taken in a quartz bucket hanging from a precision helical quartz spring enclosed in a all-glass housing. The sample was degassed at 400°C in a running vacuum of 10^{-4} torr, then cooled down in an atmosphere of nitrogen. Hydrogen was then introduced in to the system after purifying it through a deoxo catalyst maintaining a steady flow of hydrogen throughout the course of the experiment. The sample was heated at the rate of 2.5°C/min. by a precalibrated and manually operated auto-transformer. The changes in weight were observed through a micrometer-microscope. The spring balance had a sensitivity of 0.0362 mg.

Results and Discussion

Coats and Redfern⁴ derived a first order rate equation for the evaluation of thermogravimetric data of the solid decomposition reactions from the following considerations:

The rate of decomposition of a solid with temperature can be expressed by

$$\frac{d\alpha}{dT} = k(1 - \alpha)^n \quad (1)$$

where α is the fraction of the solid decomposed at time t . The rate constant, k , is given by the Arrhenius equation,

$$k = A \cdot e^{-E/RT} \quad (2)$$

where, A , E and R have usual significance. The heating rate, a , in degree/min. can be expressed as

$$a = \frac{dT}{dt} \quad (3)$$

On combining the equations (1), (2) and (3) and simplification give the following equation for a first order decomposition reaction, thus

$$\text{Log}_{10} \left[\frac{2.303}{T^2} \text{Log}_{10} (1-\alpha)^{-1} \right] = \text{Log}_{10} \frac{AR}{aE} \left[\frac{1 - 2RT}{E} \right] \frac{E}{2.303 RT} \quad (4)$$

A plot of $-\text{Log}_{10} \left[\frac{2.303}{T^2} \text{Log}_{10} (1-\alpha)^{-1} \right]$ Vs $1/T$ gives a straight line the slope of which is $\frac{E}{2.303 R}$.

Although equation (4) was derived for the first order decomposition reactions of solids in air, the same has been used in this work to study the kinetics of reduction of a nickel oxide-alumina type catalyst assuming the reduction to be a kind of decomposition of the solid in the hydrogen atmosphere.

The curve (Fig. 1A) represents the thermogravimetric data obtained during the course of temperature programmed reduction of the catalyst sample. Holm *et al*⁶ found that the reducibility of the supported nickel oxide was affected by the method of preparation, kind of support, heat treatment and promoter concentration. The difficulty observed in reducing co-precipitated catalysts was attributed to the greater opportunity for support-metal oxide interaction and also to the high degree of dispersion.

In this case, the curve (Fig. 1A) shows that only 16 per cent of the nickel oxide present in the catalyst has been reduced during the TGA run. This type of slow reduction is primarily due to the uniform distribution of the dispersed component on the alumina surface. The sample heating rate might also have some positive influence on the degree of reduction. Bandrowski *et al*² found that the rate of reaction of gaseous molecular hydrogen with the nickel oxide particles would be a slow process in comparison to the nickel catalysed reduction. Moreover, the latter is not favoured in a finely dispersed catalyst, in which the nickel oxide-nickel oxide distance is large and thus the process of

reduction can be enhanced by the incorporation of trace amounts of platinum, palladium, osmium, iridium, ruthenium and copper in the catalyst⁶⁻⁸.

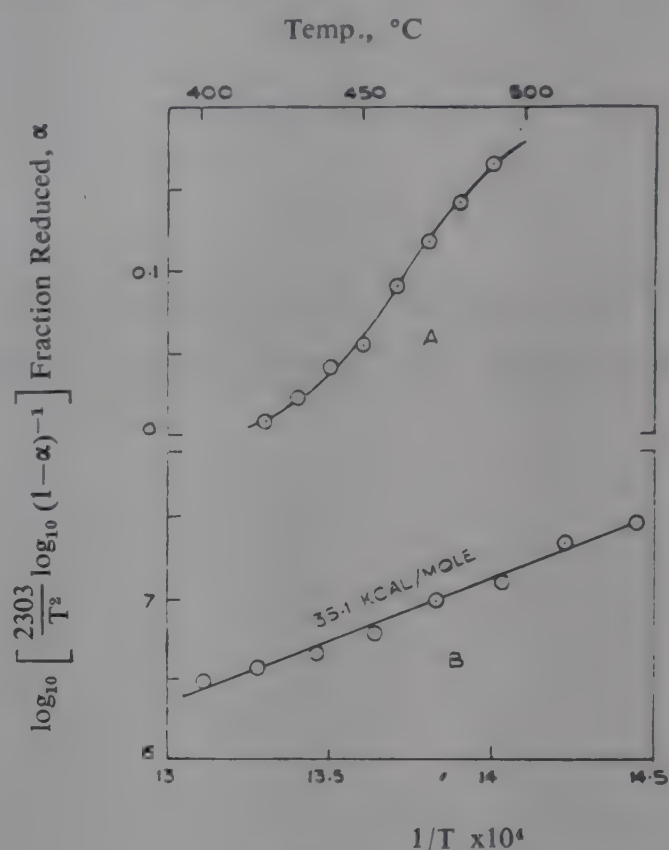


Fig. 1

The Arrhenius plot in Fig. 1B shows that the kinetics of reduction obey the first order rate equation fairly well and the apparent energy of activation is calculated to be 35.1 K. cal/mole. The present authors previously investigated³ the kinetics of reduction for a series of nickel catalysts prepared by multiple impregnation of α alumina carrier in nickel nitrate solution and found that the highly dispersed nickel oxide shows an activation energy of 27.7 K. cal/mole. Also, as the nickel concentration is increased in the catalyst, its dispersion gradually decreases and nickel oxide assumes the crystalline form on the support. As the crystalline character is developed in the supported nickel oxide, the energy of activation for the reduction also tends to approach that of the unsupported polycrystalline nickel oxide. While the observed activation energy for the finely dispersed supported material accounts for the Ni-O bond activation and also the metal-support interaction, the same for the unsupported nickel oxide (157.8 K. cal/mole) accounts for the lattice energy as well as, the bond energy.

The observed energy of activation, 35.1 K. cal/mole in the present case, therefore, may be attributed to the influence of the matrix consisting of approximately 40 per cent alpha and 60 per cent gamma aluminas respectively, to the energy of Ni-O bond activation.

Moreover, in a co-precipitated nickel catalyst the presence of a few large nickel oxide aggregates can not be ignored.

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A rapid titrimetric method using EDTA for the determination of chromium (III) as well as iron (III) and chromium in a binary system has been developed. It has been used for the estimation of the above constituents in high temperature CO-conversion catalyst. This method makes use of copper sulphate as the titrant for back titration of chromium and pyrocatechol violet, sulphosalicylic acid as indicators.

Cheletometric Determination of Iron and Chromium (III) in High Temperature CO-Conversion Catalyst

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Introduction

Direct EDTA titration procedure for the estimation of chromium (III), in spite of high stability of chromium-EDTA complex, is not feasible as chromium (III) reacts very slowly with EDTA at room temperature and chromium-EDTA complex is intensely coloured. However, previous workers¹⁻⁷ estimated chromium (III) complexometrically by back EDTA titration procedure either alone or in a binary mixture with different metal ions. For the complete formation of chromium-EDTA complex either the solution mixture was boiled for a considerable time or some catalyst, like sodium bicarbonate nitrite or sulphite, etc., added to accelerate the rate of reaction of chromium (III) with EDTA at room temperature. In back titration procedures,⁹⁻¹⁰ various metal ion solutions and metallochromic indicator pairs have been tried but most of them have limitations either in respect of the titrable amount of chromium (III) or in detection of end-point.

In the present study it has been observed that copper solution/pyrocatechol violet pair is more suitable for back titration of chromium (III) and specially for chromium (III) and iron (III) mixtures than any other pair used earlier. The method has been successfully applied for the estimation of iron (III) and chromium (III) in high temperature CO-conversion catalyst.

Experimental

The reagents used in the present study were all of AnalaR quality. The following solutions were used:

0.05M EDTA, 0.05M copper sulphate, 0.1 per cent pyrocatechol violet, 1 per cent sulphosalicylic acid in ethanol, hydrochloric acid (1:1), 5N sulphuric acid and 10 per cent hydrogen peroxide.

0.05M EDTA solution was standardized with 0.05M copper sulphate solution using pyrocatechol violet indicator. Stock solutions of chromium and iron were prepared by dissolving corresponding nitrate salts in water. All the solutions were standardized by the usual titrimetric methods.

Preparation of Catalyst Sample Solutions: About 2.0 g. of finely ground catalyst sample in each case was fused with sodium carbonate and the fused mass was dissolved in hydrochloric acid (1:1) and the volume was made up to 500 ml.

Determination of Chromium (III): To the solution containing 5 to 30 mg. of chromium (III), two to three times excess of 0.05M EDTA solution was added and diluted to 150 ml. with water. The pH of the solution was raised to 5-5.5 by adding sodium acetate/acetic acid as a buffer solution and then 0.1 to 0.2 g. solid sodium carbonate. The solution mixture was boiled for 1-2 min. and then cooled. The excess of EDTA, after addition of 5 ml. of pyridine, was titrated with 0.05M copper sulphate solution using 6 to 8 drops of pyrocatechol violet indicator to a colour change from yellow orange, red or red violet to blue, bluish-green or blue violet respectively depending on the concentra-

tion of chromium. With different concentrations of chromium the results obtained are given in Table 1.

TABLE 1—ESTIMATION OF CHROMIUM (III) IN SYNTHETIC SOLUTION

Sl. No.	Cr (III) Taken, mg.	Cr (III) Found, mg.	+ Error
1.	2.41	2.42	+0.41
2.	4.83	4.77	-0.12
3.	9.66	9.68	+0.21
4.	14.40	14.42	+0.14
5.	19.32	19.36	+0.21
6.	24.15	23.95	-0.83
7.	28.98	28.95	-0.45
8.	33.81	33.45	+1.06

Determination of Iron (III) & Chromium (III) in Synthetic Mixture: The synthetic solution containing iron and chromium was diluted to 100 ml. and its pH adjusted to about 2. The solution was titrated against a standard 0.05M EDTA solution using sulphosalicylic acid as an indicator to a colour change from dark violet to yellow green or green depending on the concentration of chromium. The volume of titrant (A) gives directly the amount of iron (III).

To another aliquot of the iron and chromium mixture, 2 to 3 times excess of EDTA solution was added followed by 1-2 g. of sodium bicarbonate and acetate buffer solution (pH 5). The excess EDTA was then titrated against 0.05M copper sulphate solution using pyrocatechol violet indicator. The volume of EDTA was thus obtained for total Iron and chromium (B). The amount of chromium was calculated from the equation: chromium (III) in mg=(B-A) f, where B is the volume of EDTA consumed by the total iron and chromium, A the volume of EDTA required for titration of iron directly, and f is the equivalent of chromium (III) in mg./ml. of 0.05M EDTA solution.

A number of synthetic solutions containing widely varying proportions of chromium and iron have been analysed following the above procedures and the results (Table 2) show that in all the cases the error is less than 1 per cent.

3. Estimation of Iron and Chromium in Catalyst Samples: An aliquot of catalyst sample solution in each case was boiled with 10 per cent hydrogen peroxide solution for 10 min. in order to reduce chromium (VI) to chromium (III) and then cooled. The determination of iron (III) and chromium (III) was carried out

as described under procedure 2. The results of all these determinations along with those by the conventional methods are given in Table 3.

TABLE 2—DETERMINATION OF CHROMIUM (III) AND IRON (III) IN MIXTURES OF EACH OTHER (Synthetic Solution)

Sl. No.	Fe(III) Taken, mg.	Cr(III) Taken, mg.	Fe(III) Found, mg.	Cr(III) Found, mg.	% Error	
					Fe(III)	Cr(III)
1.	4.22	4.80	4.21	4.83	-0.24	+0.62
2.	8.44	4.80	8.42	4.81	-0.23	+0.21
3.	4.22	9.60	4.20	9.62	-0.24	+0.21
4.	16.88	19.20	17.05	19.14	-0.89	-0.31
5.	25.32	18.20	25.20	19.14	-0.47	+0.21
6.	16.88	28.80	16.84	28.80	-0.23	0.00
7.	33.76	28.80	33.98	28.73	+0.65	-0.45
8.	42.80	24.00	42.88	24.25	+0.18	+1.04
9.	63.30	9.60	63.95	9.51	+1.02	-0.94
10.	84.40	9.60	84.91	9.52	+0.48	-0.83

TABLE 3—ESTIMATION OF IRON (III) AND CHROMIUM (III) IN HT-CO CONVERSION CATALYST

Sl. No.	+ of Fe (III)		% of Cr (III)		% Deviation	
	By Con-ventional Method	By EDTA Titration	By Con-ventional Method	By EDTA Titration	Fe (III)	Cr (III)
1.	60.06	59.05	3.65	3.71	-1.01	+0.06
2.	55.07	56.05	3.93	3.45	+0.98	+0.25
3.	60.26	60.38	3.81	2.95	+0.12	-0.86
4.	58.05	58.72	4.05	3.10	+0.67	-0.95
5.	53.50	53.81	3.98	5.01	+0.31	-1.03
6.	59.89	59.00	3.65	4.05	-0.82	+0.40

Discussion

In the present study, it has been observed that chromium reacts quickly with EDTA, if the solution mixture is warmed after adding bicarbonate. The back titration of excess EDTA has been carried out by copper/pyrocatechol since the end-point is more sharp than other titration methods, like zinc/EBT, nickel/murexide, bismuth/xlenol orange, copper/thalien, etc. Further, it has also been observed that for reduction of chromium (VI) to chromium (III) hydrogen peroxide is more suitable than sodium sulphite or other reducing agents which also reduce iron.

The estimations of chromium and iron in high temperature CO-conversion catalyst following the present procedure are found to produce results comparable with those obtained by the usual titrimetric or gravimetric methods, deviations being always within per cent for both chromium and iron. Moreover, the method is quick which is significant when frequent analyses are required.

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After grinding silica and silica-alumina gel for 1, 2, 4, 8, 16 and 24 hours, the changes in their textural properties have been studied. Their surface area decreases with increase in grinding time. The total pore volumes increased upto 1 and 2 hours in the cases of silica and silica-alumina gel respectively and then decreased, but they still remained higher than the original values. Their average pore radii and average grain diameter increased with the grinding time.

Textural Modification in Silica and Silica-Alumina Gel by Mechanical Treatment

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Introduction

The use of silica and silica-alumina gel as catalyst, catalyst support or as desiccant in industry depends mainly upon its textural properties. These properties can be modified in various ways. Several authors^{1,2} have studied the modification of silica gel properties by thermal and steam treatments under various conditions³. The chemical treatments brings about the textural changes in the silica gel⁴. The mechanical treatment of quartz and haematite results in an increase in their surface area⁵⁻⁷. Similarly, Gregg⁸ *et al* found that surface area of kaolinite increases with grinding time.

In the present investigation, the textural changes in silica, and silica-alumina gel during the process of grinding, with reference to the surface area, pore volume and grain growth have been studied.

Experimental

(A) Sample Preparation

Silica Gel: Silica gel was prepared in this laboratory by adding sodium silicate (sp. gr. 1.18) to hydrochloric acid (10 per cent), then washing the product with distilled water and drying at 110°C for 72 hr. The gel analysed as follows: loss on ignition 11.24 per cent; silica 99.1 per cent (on ignited basis); surface area 398.0 m²/g.; and total pore volume 0.6307 cc/g.

Silica-Alumina Gel: Silica-alumina gel was prepared by mixing freshly prepared silica gel suspension with a solution of aluminium nitrate and then adding ammonia solution to precipitate aluminium ions in

situ. The gel was washed till free from anions and cations, dried for 72 hours at 110°C. and then cured at 580°C. It analysed as follows: loss on ignition 1.66 per cent; Al₂O₃ 10.08 per cent; silica rest; surface area=457 m²/g.; and total pore volume 0.4466 cc/g.

The above samples were sized between 40-80 mesh (BSS) and the studies were made in the Fisher Automatic Mortar Grinder. Samples were taken after 1, 2, 4, 8, 16 and 24 hours' grinding.

(B) Measurements

Surface Area: It was measured by the usual BET method using nitrogen as adsorbate at liquid nitrogen temperature.

Pore Volume: It was determined by difference of mercury and helium displacement method.

The average pore radii and average grain diameter were calculated from the following equation.

$$r = \frac{2 V_p}{S} \dots\dots\dots (i) \text{ where}$$

2 V_p = total pore volume,
S = surface area
r = average pore radii.

$$D = \frac{6 V_a}{S} \dots\dots\dots (ii) \text{ where}$$

V_a = apparent vol. determined by Hg. displacement.
S = surface area,
D = average grain diam.

Results and Discussion

Silica Gel: The surface area of the silica gel decreased slowly with the duration of grinding which is similar to the observation of Krishentaum *et al*¹⁰. When it was ground, the surface area decreased from 655 to 599 m²/g. The total pore volume increased from 0.6307 to 0.7934 cc./g. after one hour's grinding and then it gradually fell upto 8 hours thereafter remained almost constant (Fig. 1.).

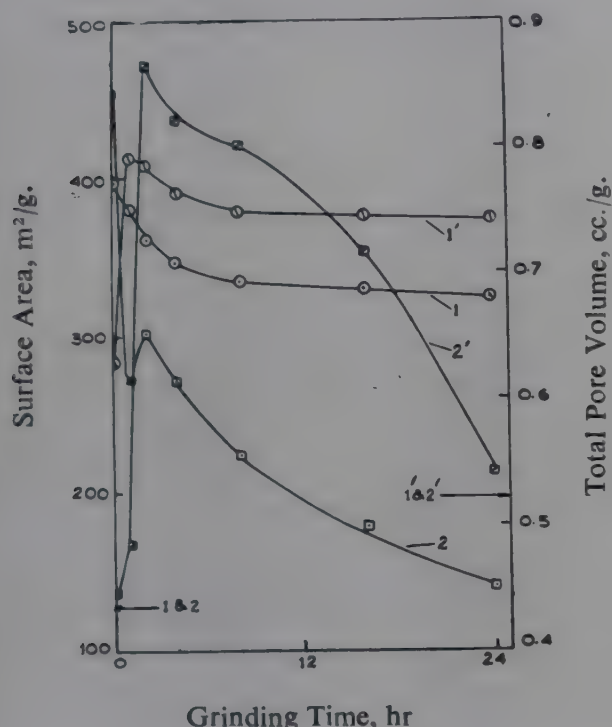


Fig. 1—Changes in Surface Area and Total Pore Volume in Silica-Alumina Gel

The average pore radii and grain diameter initially increased from 32.3 and 84.70 to 41.4 Å and 99.01 Å respectively after one hour's grinding and then increased gradually upto 8 hours, thereafter remaining almost the same.

The decrease in surface area with grinding may be due to the destruction of the original particles to finer size, which agglomerated giving rise to secondary particles having greater average diameter and average pore radii (Fig. 2) resulting in a decrease in the surface area⁹.

The increase in total pore volume depended upon the degree of agglomeration of the fine particles resulting from the destruction of the original particle.

Silica-Alumina Gel: A similar phenomenon was observed when the silica-alumina gel was subjected to

grinding. The surface area decreased sharply from 457 to 273 m²/g. after 1 hour and with slight increase to 303 m²/g, it started decreasing with grinding time upto say 24 hr. (Fig. 1).

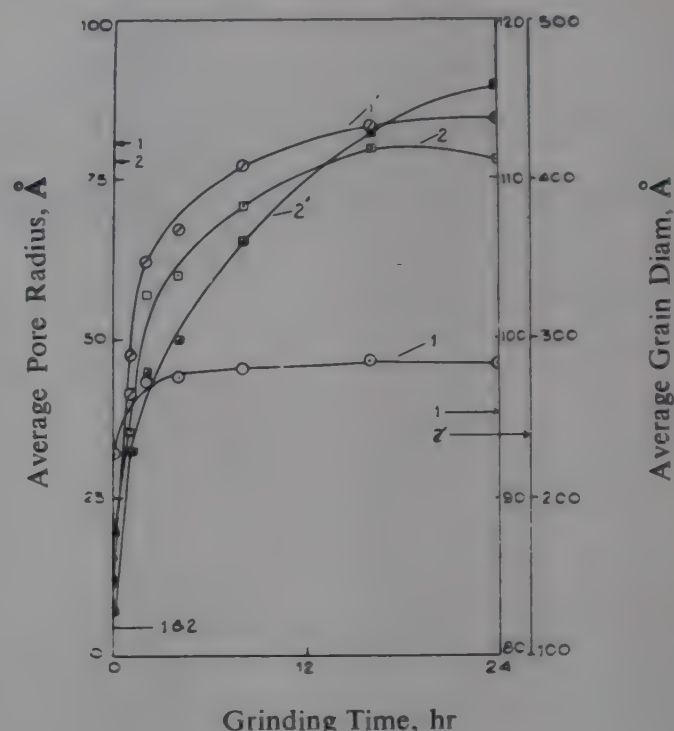


Fig. 2—Change in Average Pore Radius and Average Grain Diameter in Silica and Silica-Alumina Gel with Grinding 1 & 1' ...silica; 2 and 2' silica-alumina

Correspondingly, the average pore radii, average grain diameter and total pore volume increased sharply upto 2 hours grinding, viz. from 19.54 to 57.16 Å, 129 to 277.34 Å and 0.4466 to 0.8661 cc./g. respectively (Fig. 2). Later, the increase in average pore radii and average grain diameter were gradual, while the total pore volume tended to fall, but even after grinding for 24 hours the total pore volume remained higher than the original pore volume.

It was observed (Fig. 3) that during grinding, the samples of silica-alumina absorbed moisture from the atmosphere. The moisture varied from 1.66 per cent in the original sample to 13.89 per cent after 1 hour's grinding but on further grinding there was no regular increase or decrease in the moisture absorption. Silica gel grinding showed no such behaviour of water absorption from the atmosphere. This may be because the sample of silica-alumina on curing at 580°C was in active state, while the silica dried at 110°C, having moisture content of the order of 11.24 per cent which after grinding remained 11.98 per cent.

Conclusion

The textural properties of silica and silica-alumina can be modified to a certain extent by controlled grinding, but for a drastic achievement in textural properties, a controlled thermal or steam sintering process will be useful.

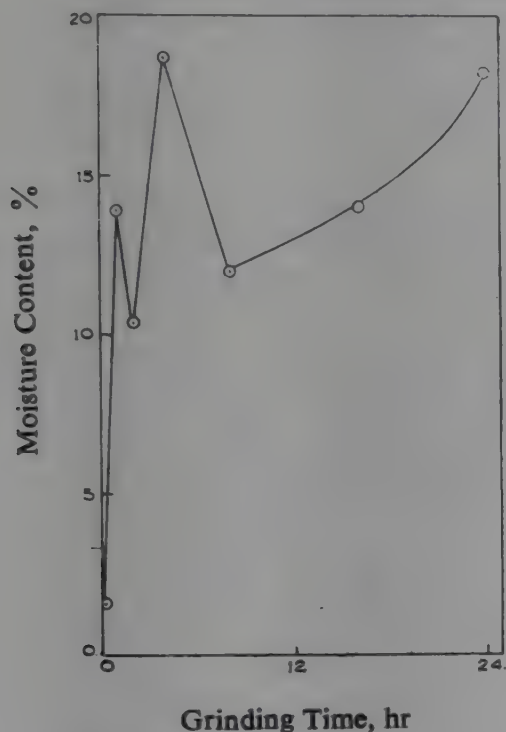


Fig 3—Change in Moisture Content of Silica-Alumina with Grinding Time

Acknowledgement

The author is thankful to Sri D. K. Gupta, Asstt. Technologist, for determining the surface area of the samples.

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The preparation and stoichiometry of complex compounds of biuret formed with metals, like Cr (III), Fe(III), V(III), Ag(III), UO_2 (II) and Cu (II) (mixed ligand), are reported.

An Appraisal of Biuret-Metal Interactions

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In the previous communications¹⁻⁵, complexing as well as other physico-chemical properties of biuret have been elaborately discussed. The potentiometric titration data for some of the bivalent metal ions with biuret suggest the 1:2:: metal: biuret ratio in solutions⁶. The chemical nature of biuret complexes specially with the bivalent metals are studied by different workers⁷⁻⁸. With biuret some more di- and tri-positive metal ions, viz. Cu(II), UO_2 (II), Cr(III), Fe(III), V(III) and Ag(III) are found to form coloured metal biuret chelates in acidic, neutral and alkaline medium. The stoichiometry of metal complexes in all the cases in the present study is metal: ligand::1:1 (in solution) except in vanadium and silver where 2:3 and 1:2 stoichiometry are observed respectively. The mixed ligand complexes (with biuret, ammonia and pyridine) also prepared with Cu(II) metal ion.

Experimental

Biuret used in this experiment was of AnalaR grade reagent and other metallic salts and reagents used were reagent grade or equivalent.

Preparation: Mostly the complexes are prepared by mixing metal: ligand in equimolar ratio 1:4. pH of the mixture was measured. The content was refluxed on a water bath for complete reaction. The solid compounds were isolated from the solution and were washed with water, alcohol and finally with acetone. The compounds were dried in vacuum dessicator over fused calcium chloride. In case of Ag(III) complex oxidation of metal nitrate was carried out by potassium persulphate.

Analysis: The estimation of metal ions was carried out by standard method. The nitrogen analysis was also done by Kjeldahl's method.

TABLE 1—ANALYTICAL DATA FOR BIURET COMPLEXES

Metal Ions	Metal: Biuret Ratio	Proposed Formula	pH	Colour	Solubility	M.P., °C	Analysis			
							%Metal		%Nitrogen	
							Found	Required	Found	Required
Cu(II)	1:1	$[\text{Cu}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)(\text{NH}_3)(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$	9.0	Muddy green	Insoluble	198	24.93	25.05	22.00	22.09
Cu(II)	1:1	$[\text{Cu}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)(\text{C}_5\text{H}_5\text{N})(\text{H}_2\text{O})]$	10.0	Light	Insoluble	Decomp. 201	24.35	24.27	22.00	21.40
UO_2 (II)	1:1	$[\text{UO}_2(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$	3.0	Orange	Insoluble	Decomp. 200	44.89	45.19	8.03	7.97
Cr(III)	1:1	$[\text{Cr}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)\text{OH}(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}$	11.0	Green	Water	Decomp. above 230	17.01	17.57	14.32	14.19
Fe(III)	1:1	$[\text{Fe}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)\text{Cl}_3] \cdot 4\text{H}_2\text{O}$	3.0	Reddish brown	Ethanol	Decomp. above 250	18.58	18.66	13.92	14.04
V(III)	2:3	$[\text{V}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_3] \cdot \text{VO}_4$	5.0	Orange	Insoluble	Decomp. above 260	21.82	21.44	26.72	26.53
Ag(III)	1:2	$[\text{Ag}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_3](\text{NO}_3)$	8.0	Brownish yellow	Partly soluble in water	Decomp. above 200	21.44	21.58	25.21	25.21

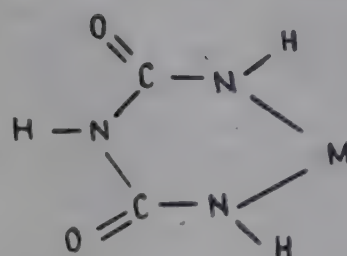
Results and Discussion

The analytical data in Table 1 gives the stoichiometry, pH, solubility, melting point and proposed formula for the biuret metal-chelate compounds. In the case of vanadium (III)-biuret complex it has been observed that vanadium (V) reduces to vanadium (III) after complexing with biuret. Thus, biuret may work as reducing agent in certain condition. As regard the solubilities it has been observed that the complexes of copper (II), vanadium (III) and UO_2 (II) are insoluble in water whereas chromium (III) complex is soluble in water but insoluble in organic solvents. The iron (III) complex is soluble in alcohol and partly soluble in water. The molar conductance of the iron (III) biuret compound in ethanol solution comes out to be 4 mhos, indicating non-electrolytic nature of the complex at room temperature. The compound also slowly hydrolyses in the aqueous solution. The silver (III) complex is sparingly soluble in water and conductivity measurement of the complex (410 mhos) indicates the presence of tripotassium cation on dissociation.

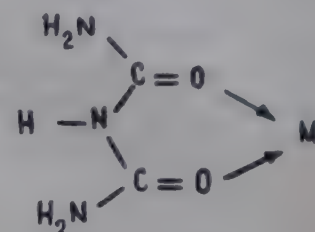
In biuret, coordination occurs mainly through two oxygen of the carbonyl groups and two nitrogen of the amide groups, depending on the acidic and alkaline medium⁷. In the case of copper (II)-(ammonia)-biuret, copper(II)-(pyridine)-biuret and chromium(III)-biuret complexes which are found in alkaline medium may be coordinated through two nitrogen of amide groups (structure I). The complexes formed in acid or neutral medium like vanadium (III), iron (III), silver (III) and UO_2 (II) may be coordinated through

oxygen of the carbonyl ($\text{C}=\text{O}$) groups (Structure II). Thus, the proposed structure may be written as follows:

Structural Formulae



Structure I



Structure II

where M stands for bi- or trivalent metals.

Further studies for complete elucidation of electronic, magnetic along with structural properties are in progress.

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Magnetic studies were performed on some iron-chromium alloys prepared by amalgamation process. These studies show the alloys to have gradually decreasing exchange interaction with increasing chromium atomic percentage. Excepting a minor secondary phase in one of the alloys and one peculiar and completely reversible transition, Curie point observations show a monotonic decrease with increasing chromium atomic percentage. The observations on the saturation magnetic moment reveal the futility of the extrapolation process of the straight line variation reported earlier for higher chromium percentages for the present binary alloy system. The linear lattice parameters instead of the chromium atomic percentage is taken as the independent variable.

Magnetic Studies of Some Iron-Chromium Alloys Prepared by Amalgamation Process

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The effect of compositional and structural changes on the energy distribution of the electrons is manifested in the magnetizations of ferromagnetic transition metal alloys. The magnetic studies are therefore essential for the determination of the electronic structures of the transition metal alloys. Further in order to study the causes of the sluggish solid state transformations generally observed in some transition metal binary alloys at lower temperature ranges, a full understanding of the phase composition and of the structural state of equilibrium must be obtained for the alloy system prepared at low temperatures. This paper presents magnetic studies of some iron-chromium binary alloys prepared by the amalgamation process. The x-ray data for these samples have already been reported¹. Some relations between the ferromagnetic exchange interaction with the substitutional characteristics of the chromium atoms in the body centred cubic lattice of iron from their magnetic studies have been tried to be found out.

Fallot² reported data for saturation magnetic moments for these alloys for the chromium atomic percentage range from 17.7 to 68.8. The samples were prepared by melting at high temperatures and by subsequent heat treatments. Nevitt and Aldred³ reported similar data for the chromium percentage range from 80.0 to 86.0 for samples prepared by induction melting at high temperatures in alumina crucibles and later giving proper heat treatments to the alloys.

Nevitt *et al*³ proposed a linear variation of the saturation magnetic moment with atomic fraction of iron in these alloys on the basis of their experiments. These experiments, however, were not performed on alloy containing low percentages of chromium. Considering the complexity of the exchange interaction, which involves not only the nearest neighbours, but the more distant atoms as well, the linear variation model proposed by Nevitt *et al* appears insufficient. The present study was undertaken to ascertain the true nature of such variation, extending the scope to cover the region of lower chromium concentration, where departures from the apparent linearity, if any, should be more obvious.

Experimental

Measurements were performed with a servo-type self-balancing magnetic balance⁴. The alloys were sealed in vacuum in small needle shaped capsules made of quartz in order to prevent oxidation of the alloys at high temperatures. This particular shape of the samples was taken to reduce the demagnetising field. Saturation magnetic moment and magnetic hardness of the alloys were measured following the method described earlier. The Curie points obtained for these alloys are given in Table 1.

The saturation magnetic moment as functions of chromium atomic percentage for these alloys at three different temperatures are plotted in Fig. 1. Fig. 2

shows the relation between saturation magnetic moment and lattice spacings of the respective alloys determined by x-ray analysis. Fig. 3 shows the plots of magnetic

TABLE 1

Chromium, atomic %	Iron, atomic %	Ferromagnetic Curie Point, °C.
0	100	770
5	95	745, 770 (minor)
10	90	755
20	80	745
30	70	720, 760
40	60	495

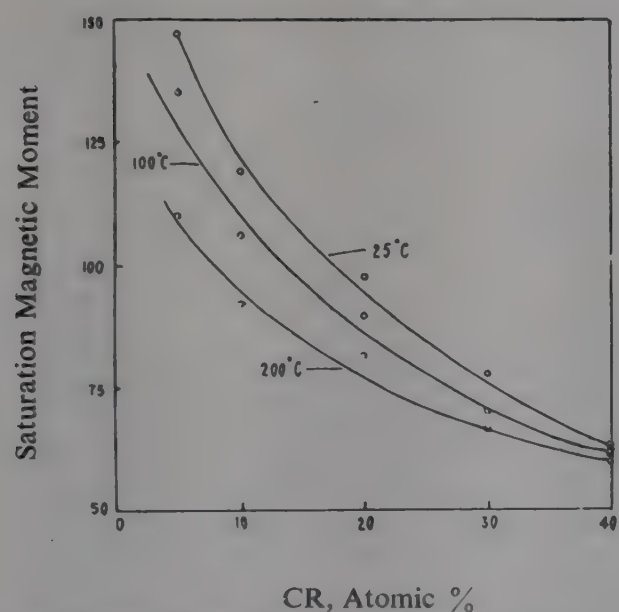


Fig. 1—Plot of Saturation Magnetic Moment Against Chromium Atomic Percentage at Three Temperatures

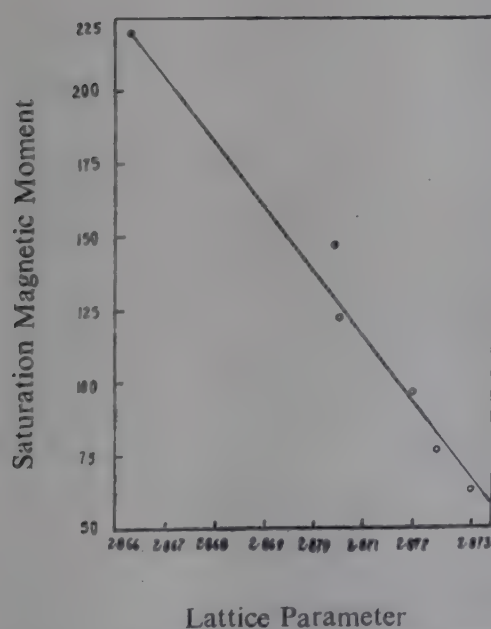


Fig. 2—Plot of Saturation Magnetic Moment Against Lattice Parameters at 25°C

hardnesses against chromium percentages of the alloys at three different temperatures.

Discussion

The Curie points of these alloys show in general a decrease with increasing chromium percentages but the variation is in no way linear. In 5 per cent chromium alloy minor quantities of a secondary phase having identical Curie point as that of iron was detected. It has been reported that a change in the lattice parameter has been observed in case of 7 per cent chromium alloys prepared from the melt. It is possible that energetically, it represents a minimum, and the 5 per cent Cr alloy prepared from amalgam as was studied in the present work, might not have attained complete stability at high temperature. The 30 per cent chromium alloy revealed one very peculiar behaviour of showing one single Curie point transition at 760°C while heating whereas it showed two distinct Curie points while cooling. This effect was also found to be completely reversible. This thermal hysteresis might indicate the possibility of the chromium atoms switching over between two types of sites in the lattice of iron thereby altering the ferromagnetic exchange interaction.

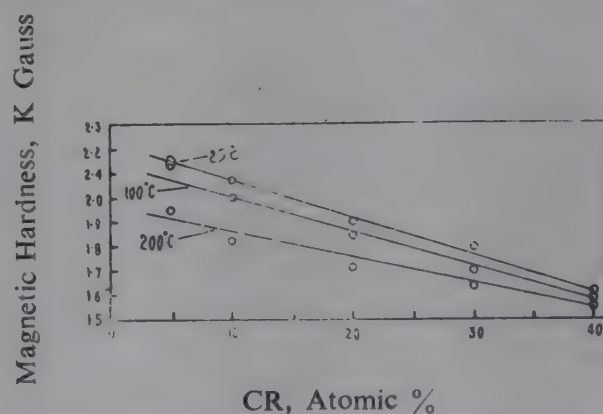


Fig. 3—Plot of Magnetic Hardness Against Chromium Atomic Percentage at Three Temperatures

The nature of variation of saturation magnetic moment of these alloys showed monotonic decrease at all temperatures with increasing chromium percentages. The data obtained also suggest appreciable departures from the linear variation observed for higher chromium atomic fraction in iron-chromium binary alloys by the previous investigators^{1,2}. The departure from the straight line becomes more and more marked as chromium atomic fraction is decreased. Another important observation is the variation of saturation magnetization which approximates more towards straight line when similar plots are tried against lattice spacings as abscissa as is easily evidenced from Fig. 2. The magnetic hardness shows approximately a linear increase with decreasing chromium percentages.

Acknowledgements

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Various types of interferences which may affect the determination of trace elements, viz. cobalt, copper and zinc, by the atomic absorption method have been dealt. It has been found that estimation of these essential micronutrients in soils is mainly affected by light scattering effect. A simple digestion method has been used for sample preparation and the above effect has been accounted for.

Interferences in the Estimation of Trace Amounts of Cobalt, Copper and Zinc in Soils by Atomic Absorption Spectrophotometry

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Introduction

The important role played by micronutrients in soils is well-known. Some trace elements present in soils from different parts of the country were estimated¹ in this laboratory using a spectrographic technique, wherein three essential micronutrients, viz. cobalt, copper and zinc, could not be determined. Copper present in traces in all the samples, could not be estimated due to interference from manganese and titanium, while cobalt and zinc could not be detected, probably because their amounts present were very low or their spectral lines were suppressed² by some extraneous materials in the samples. So their estimation has been undertaken using atomic absorption technique.

In the early days of atomic absorption spectrometry, it was claimed that, in general, this method was free from interferences. Later, it was found that analysis of a number of elements may be affected by different interferences, e.g. spectral, excitation, ionization, chemical and light scattering interferences. The first two types of interferences are rare in atomic absorption and the ionization interference is generally observed in case of alkali metals and some of the alkaline-earth.

Chemical interference is probably most important and predominant in atomic absorption. As regards the interference on cobalt, copper and zinc, Sachdev *et al*³ found no interference with cobalt absorbance

for a number of cations and anions except in excess of 2000 ppm. Varju⁴ demonstrated that 2000 ppm of aluminium, iron, calcium, sodium, potassium and magnesium ions do not interfere with copper determination. Slight or insignificant interference was observed from a number of cations and anions on the estimation of copper⁵⁻⁶ and zinc⁵⁻⁷ by some workers. We found practically no chemical interference upto 1000 µg./ml. of aluminium, iron and calcium and upto 500 µg./ml. of sodium, potassium and magnesium on the determination of cobalt, copper and zinc at the levels they are present in the working solutions.

Light scattering is an interference observed in the analysis of trace elements in solutions with high solid content. This is caused by the scattering of some light by the salt particles which are not vaporized and survive in the flame. This results in an apparent increase in the absorption by a particular element in the solution. David⁸ reported this effect, whereas Billings⁹ studied it in some detail. The magnitude of the scattering effect varies considerably and is severe at short wave lengths, especially below 3000 Å. Ure and Mitchell¹⁰ observed this effect while determining cobalt in soil extracts. Willis¹¹ suggested that this effect can be corrected by analysing the sample at a line close to the analytical line but non-absorbing (i.e. a line where no absorption is observed when aspirating a dilute solution containing small quantities of the analyte) and subtracting the background absorption from the total

absorption obtained at the analytical line. This method has been followed here for correction of this effect which was observed in the case of cobalt and zinc estimations.

For the determination of trace elements, extraction methods¹²⁻¹⁵ have been generally used for their enrichment before they are estimated by the atomic absorption technique. These methods are lengthy and time-consuming. In the present work, the three micro-nutrients, viz. cobalt, copper and zinc, have been estimated quickly and accurately using a digestion process similar to that suggested by Jackson¹⁶. No enrichment of the samples was required. As no chemical interference was observed, only light scattering effect was taken into account and a correction has been made as suggested by Willis¹¹.

Experimental

Equipments: A Perkin-Elmer model 303 atomic absorption spectrophotometer, equipped with a burner head for air-acetylene flame and hollow cathode lamps of copper and zinc and a multi-element hollow cathode lamp for cobalt, was used. The zinc hollow cathode lamp went out of order on the expiry of its life, so it was used after reactivation by the method suggested by Sinha *et al*¹⁷. The analytical lines of cobalt and zinc fall in the ultraviolet region and so the three windows of the instrument were removed to avoid absorption of light by them, thereby increasing the sensitivity. For the study of chemical interference, a λ -shaped double capillary aspiration system (DCAS-1:1) designed in this laboratory¹⁸ has been used in place of the usual single capillary.

Sample Preparation: The seven soil samples taken up for the earlier work¹ were finely powdered and oven-dried. 1.0 g. of each sample was taken in a clean platinum crucible, moistened with a few drops of distilled water and 2 drops of sulphuric acid added. 5 ml. of hydrofluoric acid was then added and the contents were evaporated to dryness at about 200°C on a sand bath. A further addition of 5 ml. of hydrofluoric acid was made and evaporation repeated to get rid of the silica in the sample. Now, 10 ml. of concentrated nitric acid was put into the crucible which was kept in a 250 ml. beaker. The crucible was covered with distilled water and heated. The mass was then transferred to the beaker. The solution was evaporated to dryness and 10 ml of an acids mixture (6 ml. nitric acid + 3 ml. perchloric acid + 1 ml. sulphuric acid) was added to the residue in the beaker and organic material in the soil was destroyed by evaporating the acids to dryness. The residue was

taken in 10 ml. of distilled water containing 1 ml. hydrochloric acid by mild boiling on a hot plate. The contents were cooled, filtered and volume made to 25 ml. Similarly, other sample solutions were prepared. A blank was also made using the same process except that no sample was taken in the crucible.

The above solutions were directly used for the estimation of cobalt and copper. For zinc, these solutions as well as the blank were diluted 5 times.

Standard Solutions: For the preparation of standard solutions, 1 per cent stock solutions of the above elements (from M/s. Harleco, USA) were used. Three standards each for cobalt (1, 2 and 3 μ g./ml.), copper (1, 2 and 5 μ g./ml.) and zinc (1, 2 and 3 μ g./ml.) were prepared by successive dilution of the above stock solutions with distilled water. The hydrochloric acid content in the standards was kept same as that in the sample solutions.

For studying the interference effect, standard solutions of 4 μ g./ml. of cobalt and copper and 1.6 μ g./ml. of zinc were made from the stock solutions. Also solutions of the major elements containing 500, 1000 and 2000 μ g./ml. respectively of aluminium, calcium and iron and 250, 500 & 1000 μ g./ml. respectively of sodium, potassium and magnesium were made for use with DCAS (1:1).

TABLE 1—EXPERIMENTAL CONDITIONS

Element	Cobalt	Copper	Zinc
Wavelength, Å	2407	3247	2139
Slit width, mm.	0.3	1.0	1.0
Source current, mA	35	15	25
Scale expansion	$\times 2$	—	—
Meter response	3	2	3
Flame	Oxidizing	Oxidizing	Oxidizing
Pressure, psi			
Air	30	30	30
Acetylene	8	8	8
Flowmeter reading			
Air	9.0	9.0	9.0
Acetylene	9.0	9.0	9.0

Procedure: The instrumental conditions (Table 1) for the three elements, viz. cobalt, copper and zinc, were set similar to those given by Perkin-Elmer¹⁹, after removing the three covering windows of the instrument. In the case of zinc (reactivated lamp) higher current setting was required.

For observing the interference by the major elements on cobalt, the two lower capillaries of DCAS (1:1) were dipped in distilled water and zero of the instru-

ment adjusted while aspirating water into the air-acetylene flame. Now one end was dipped in 4 μ g./ml. solution of cobalt while keeping the other one in the distilled water and absorption due to 2 μ g./ml. cobalt solution (as the 4 μ g./ml. solution is diluted in the ratio 1:1 when aspirated through one lower capillary of the double capillary system) was noted. Now keeping one capillary in the cobalt solution, various standards of the major elements (which will also get diluted in the ratio of 1:1 as cobalt) were aspirated one after the other through the other capillary and corresponding per cent absorptions were noted. Similarly, the 4 μ g./ml. solution of copper was aspirated through one capillary and standards through the other and interference study was made on 2 μ g./ml. copper. In case of zinc, 1.6 μ g./ml. solution was aspirated for the above study. In all the cases, practically no change was observed in the per cent absorption. This showed the absence of any significant chemical interference due to aluminium, calcium and iron upto 1000 μ g./ml. and sodium, potassium and magnesium upto 500 μ g./ml. respectively.

For the estimation of the three micronutrients, the zero of the instrument was adjusted by aspirating distilled water through a single capillary into the flame. The standards were then aspirated and their corresponding per cent absorptions were read from the absorption counter. Now the zero was adjusted with the blank solution and absorption values determine for the samples. A scale expansion of X 2 was used in the case of cobalt, whereas for copper and zinc readings were taken directly. As light scattering effect was observed in the case of cobalt and zinc, per cent absorptions were noted for the sample solutions at non-absorbing lines, viz. 2380 $\text{\AA}$ for cobalt and 2160 $\text{\AA}$ for zinc respectively, and subtracted from the corresponding absorptions at the analytical lines to get the actual per cent absorption. In the case of copper, this effect was absent. From the calibration curves (Figs. 1 & 2), the amounts of the three elements were noted and the corresponding contents in soil samples are given in Table 2.

Results and Discussion

The digestion method used for the present work was quite satisfactory. By hydrofluoric acid treatment, silica which is a base in soils was removed. This avoided any interference by silica on the estimation of the three trace elements. It also allowed us to take a larger amount of sample, viz. 1 g. soil in 25 ml. of solution (i.e. 4 per cent solution but due to the re-

TABLE 2—CONTENTS OF COBALT, COPPER AND ZINC IN SOME INDIAN SOILS, PPM

Sl. No.	Soil Sample from	Cobalt	Copper	Zinc
1.	Amraoti	30.5	113.0	48.7
2.	Jodhpur	3.0	6.2	n.d.
3.	Ludhiana	3.0	16.7	38.7
4.	New Delhi	n.d.	20.5	76.2
5.	Sindri Farm	10.0	41.7	66.2
6.	Sindri (Rangamati)	10.5	14.2	18.7
7.	Chaibasa	27.5	76.2	32.5

n.d.—not detected

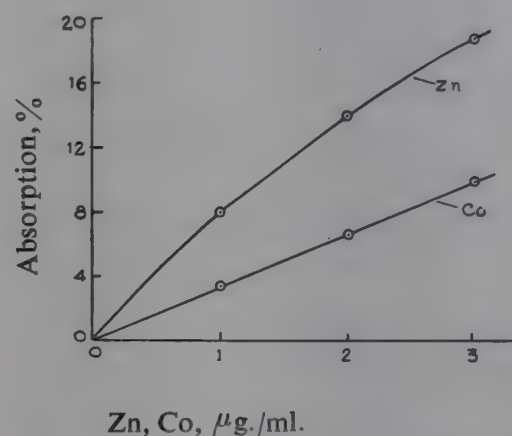


Fig 1—Calibration Curve for Zine and Cobalt

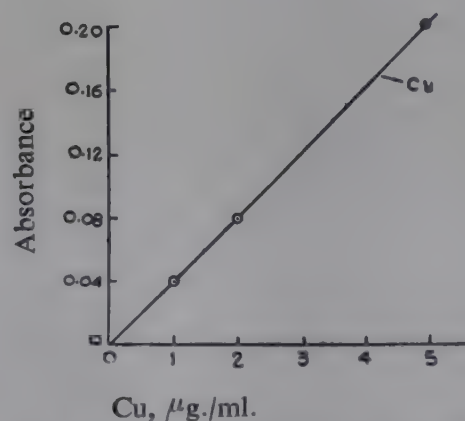


Fig 2—Calibration Curve for Copper

moval of silica the actual solid content in the solution was less than 1 per cent) and so preconcentration or enrichment step, which is generally used in trace element determination, was avoided.

Practically no chemical interference was observed from the major elements present in the sample solutions. In case of copper estimation, the light scattering effect was also absent. In case of cobalt and zinc determinations, light scattering effect was observed and was accounted for.

From Table 2, it is obvious that the contents of all the three micronutrients vary from soil to soil from different places. Cobalt was not detected in New Delhi soil whereas zinc was not present in the Jodhpur soil. In addition to these three trace elements and those determined earlier¹, there are two other essential micronutrients, viz. molybdenum and boron, which could not be estimated in the present work as they require a high temperature nitrous oxide-acetylene flame, which was not available.

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Particle size analysis in the sub-sieve range has been done by sedimentation in the calcium carbonate slurries deflocculated by sodium polyphosphates and some ammonium and alkali metal salts. Reduction in the viscosity of the slurries has been found to be attended by a general decrease in the effective size of the particles. It has been observed that the size distribution also contributes in lowering the viscosity.

Changes in Particles Size in the Deflocculated Calcium Carbonate Slurries

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The effects of addition of sodium polyphosphates and some ammonium and alkali metal salts on the viscosity of slurries of calcium carbonate—both chemically pure and the by-product samples—have been reported in previous communications^{1,2}. A change in particle size being an important factor accompanying the change in viscosity of the slurries³⁻⁷, the slurries of calcium carbonate after treatment with additives were subjected to particle size analysis by sedimentation, particularly to compare the effects of sodium polyphosphate prepared here and the other commercially available ones. The results have been reported in this communication.

Experimental

Particle size analysis in the sub-sieve range was carried out by sedimentation on a Gallenkamp sedimentation balance PC-650. A portion of the finally deflocculated slurry containing about 0.5-1.0 g. of solid was weighed and passed through a -200 mesh (BSS) sieve. The -200 mesh portion was suspended in 250 ml. distilled water and 225 ml. of it was taken in the special mixing tube. After a thorough agitation the sample was transferred to the sample container of the balance.

The initial reading was taken after 15 sec. of transference of the sample and the succeeding readings at time increasing by a factor of $\sqrt{2}$ up to 362 min. 40 sec. and up to the final constant reading. The results were calculated from the following relationship given by Bostock⁸:

$$W = P - \frac{d P}{d (\log_e t)},$$

where W is the percentage of particles greater than a chosen diameter and P is the percentage settled weight at the time t. The curves of P against $\log_e t$ were drawn and differentiated graphically at every half unit of $\log_e t$, and plots of the differential were also made against $\log_e t$. The particle fall times corresponding to the chosen diameters were calculated from the Stokes law:

$$t = \frac{18 h \eta}{(D_2 - D_1) d^2 g}$$

where t = time for particles to fall the full depth of the suspension, sec.

h = depth of suspension, cm.

D_2 = density of suspended solid, g./ml.

D_1 = density of liquid, g./ml.

d = Stokes diameter of particles, cm.

g = acceleration of gravity, cm./sec².

η = viscosity of liquid, poise.

The times were chosen to allow for the fall through the full length of the suspension of the sizes 50, 30, 20, 10 and 5 μ . The corresponding values of $\log_e t$ were noted and the difference between the ordinates gave the percentage weight of particles greater than the particular size. The figure obtained for 50 μ gave the percentage weight greater than 50 μ . The figures for the lower ranges were obtained by difference between

TABLE 1—DEFLOCCULATION OF CALCIUM CARBONATE (B. D. H.) SLURRY BY SODIUM POLYPHOSPHATE

20% w/w Slurry					25% w/w Slurry				
Polyphosphate, g./100 g. slurry	Viscosity in Cp at 35°C Reduced by				Polyphosphate, g./100 g. slurry	Viscosity in Cp. at 35°C Reduced by			
	Sample 1	Sample 2	Sample 3	Sample 4		Sample 1	Sample 2	Sample 3	Sample 4
0.0	400	400	400	400	0.0	950	950	950	950
0.1	140	160	150	70	0.1	680	450	540	180
0.2	40	55	105	10	0.2	150	140	400	15
0.3	20	35	50	—	0.3	50	100	250	—
0.4	10	20	35	—	0.4	40	70	150	—
0.5	—	—	20	—	0.5	50	80	110	—
					0.6	—	—	100	—
					0.8	—	—	90	—
					1.0	—	—	90	—

TABLE 2—EFFECT OF SOME SALTS ON THE VISCOSITY OF CALCIUM CARBONATE (B. D. H.) SLURRIES

Salt, g./100 g. slurry	Viscosity of 20% w/w Slurry at 35°C, Cp.								
	(NH ₄) ₂ SO ₂	NH ₄ Cl	NH ₄ NO ₃	KCl	K ₂ SO ₄	KNO ₃	NaCl	Na ₂ SO ₄	Na ₂ HPO ₄ · 12H ₂ O
0	400	400	400	400	400	400	400	400	400
1	250	370	340	350	330	370	390	300	350
2	220	350	305	330	290	350	360	250	350
3	190	300	290	320	280	310	340	240	330
4	150	290	270	305	260	290	315	220	310
6	110	270	250	275	220	250	290	190	230
8	100	250	220	225	220	230	260	150	200
10	95	210	200	205	—	215	240	140	180
12	90	160	180	185	—	185	220	130	160
14	—	125	160	165	—	—	—	120	155
16	—	105	145	150	—	160	190	110	150
20	—	75	110	120	—	140	170	90	—

TABLE 3—PARTICLE SIZE IN CALCIUM CARBONATE SLURRIES AFTER DEFLOCCULATION WITH SODIUM POLYPHOSPHATE

Particle Size Range, μ	Undefloc- culated Slurry, %	20% w/w Slurry, % in size range				25% w/w Slurry, % in size range			
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 1	Sample 2	Sample 3	Sample 4
>50	29.0	—	1.0	—	—	—	—	—	—
50-30	44.0	1.0	1.0	1.5	1.0	0.5	1.5	1.0	1.0
30-20	16.0	4.1	3.0	2.0	3.5	2.0	3.5	3.5	4.5
20-10	7.0	29.9	17.0	32.5	25.5	31.5	42.5	20.0	44.0
10-5	3.0	50.0	53.0	45.0	54.0	62.5	44.0	60.0	39.0
<5	1.0	15.0	25.0	19.0	16.0	3.5	18.5	15.5	11.5

TABLE 4—PARTICLE SIZE IN CALCIUM CARBONATE SLURRIES AFTER TREATMENT WITH SOME SALTS OF AMMONIUM, SODIUM AND POTASSIUM

Particle Size Range, μ	Undefloc- culated Slurry, %	20% w/w Slurry Treated with								
		(NH ₄) ₂ SO ₄	NH ₄ Cl	NH ₄ NO ₃	KCl	K ₂ SO ₄	KNO ₃	NaCl	Na ₂ SO ₄	Na ₂ HPO ₄ · 12H ₂ O
>50	29.0	23.0	17.5	13.5	16.5	18.0	15.0	17.0	23.0	16.0
50-30	44.0	35.0	37.5	21.5	23.0	32.5	27.5	27.0	35.0	42.5
30-20	16.0	30.0	34.5	49.5	50.0	38.0	37.0	30.0	26.0	33.0
20-10	7.0	7.0	6.0	11.5	5.5	8.5	17.0	20.0	10.0	7.0
10-5	3.0	5.0	3.0	3.0	2.5	3.0	3.5	6.0	6.0	1.5
<5	1.0	—	1.5	1.0	2.5	—	—	—	—	—

the adjacent sizes and the less than 5 μ fraction by difference from 100.

Results and Discussion

The results of deflocculation of calcium carbonate slurries by different samples of sodium polyphosphate and those by different ammonium, sodium and potassium salts (Tables 1 & 2) are reproduced from earlier communications^{1,2} for comparison with the results of particle size determinations in the corresponding slurries which have been tabulated in Tables 3 and 4 respectively.

In the case of polyphosphates the effectiveness of deflocculation was in the order of sample 4 > sample 1 > sample 2 > sample 3. The minimum values of viscosity attained in 20 per cent w/w slurry were comparable in samples 1 and 4 on one hand and samples 2 and 3 on the other, whereas in 25 per cent w/w slurry the minimum values of viscosity attained were in the order of effectiveness of deflocculation. The distribution of particle size ranges were also quite closely comparable in slurries treated with samples 1 and 4, the percentage of smaller size range (10-5 μ) being slightly higher in sample 4. The percentage of size ranges was more varied in sample 2 than in sample 3 and also the percentages in the lower size ranges (10-5 μ and < 5 μ) were higher in sample 2.

In the 25 per cent w/w slurry, the maximum percentage of 10-5 μ size range was in sample 1 and then in sample 3. The distribution in the lowest three size ranges, viz. 20-10, 10-5 and < 5 μ , were roughly comparable in samples 2 and 4, the 10-5 μ percentage being slightly lower and that of < 5 μ slightly higher than the corresponding figures in sample 2.

The effectiveness of the various salts of ammonium, sodium and potassium is in the following order: ammonium sulphate > ammonium nitrate > potassium chloride > potassium nitrate > sodium chloride > disodium phosphate. The results of the particle size distribution showed that there is general reduction in the particle size but the increase in the size ranges below 20 μ was not appreciable. In the case of deflocculation by different sulphates, the simultaneous formation of calcium sulphate in small amounts also helped in reducing the viscosity, which might be responsible for greater effectiveness of the sulphates¹.

Thus, in the deflocculation of calcium carbonate slurries by different additives used, the viscosity reduction was attended by a general decrease in the effective size of the particles as found by sedimentation. Similar observations were made in the case of gypsum slurries⁹ and also by other workers working with different suspensions^{10,11}. De-aggregation^{12,13} and decrease in hydration^{14,15} of the sols have also been reported to cause decrease in viscosity.

The results (Tables 3 and 4) further indicated that in addition to the reduction to smaller sizes, the size distribution also has a contribution in lowering the viscosity. These observations conformed to the observations of other workers¹⁶⁻¹⁹.

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The effect of various oxidizing agents on the cation-exchange resin, Sindex-C26, has been studied and the results have been compared with a polystyrene sulphonated cation-exchange resin, Dowex-50W $\times$ 8. The effect of chlorine has been studied, particularly in detail.

Effect of Oxidizing Agents on Cation-Exchange Resin, Sindex—C26

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The behaviour of ion-exchange resins varies greatly towards different oxidizing agents. Their resisting power increases with the degree of cross-linking. The condensation-type cation-exchange resins have been found to be more sensitive even to less strong oxidizing agents, because of the oxidizability of their phenolic hydroxyl groups. The chlorination of strong acid resins results in a significant decrease in number of sulphonic acid groups^{1,2}.

The effect of oxidizing agents on the capacities and moisture content of Sindex-C26^{3,4} a cation-exchange resin produced from waste acid sludge, was studied. The oxidizing agents selected were chlorine water, potassium permanganate and potassium dichromate but the studies in chlorine were carried out in detail. For comparing the results of Sindex—C26, studies have also been made with Dowex-50 W $\times$ 8.

Experimental

Freshly prepared chlorine water was used for the purpose. All the chemicals used were of AnalaR grade.

The ion-exchange resin samples were prepared by taking each in a column and passing excess 1N hydrochloric acid through it at a slow rate. The excess adsorbed acid was washed with distilled water and the resin was converted to the sodium form by passing 1N sodium hydroxide. After washing again, the resin was converted to hydrogen form by passing 1N hydrochloric acid. After washing the sample was then ready for use and its moisture content and exchange capacities were determined. In this way, both the samples of Sindex-C26 and Dowex-50W $\times$ 8 were prepared.

Oxidation with Chlorine Water: The studies were divided mainly in the following two parts.

- (i) 5g. of air-dried samples of each Sindex-C26 and Dowex-50W $\times$ 8 were separately treated with 500 ml. of chlorine water of 0.1 N concentration and kept for one day. Then the resin samples were washed free from chlorine by water and the capacities were determined for both the samples (Table 1).

TABLE 1—CHARACTERISTICS OF ION-EXCHANGE RESIN

Details of the Resin	Sindex C26	Dowex-50W × 8	
		Experi- mental	Earlier Work ⁵
<i>Unchlorinated</i>			
(a) Moisture Content, % (w/w)	45.8	52.99	53.30
(b) Total Capacity, meq./g.	3.93	5.19	4.95
(c) Salt Splitting Capacity, meq./g.	2.23	5.10	4.90
(d) Difference in Capacity, %	43.20	1.80	1.00
(e) Bulk Density, H ⁺ Form, g.(dry)/ml.(wet).	0.36	0.38	—
<i>Chlorinated</i>			
(a) Moisture Content, % (w/w)	56.50	50.4	47.20
(b) Total Capacity, meq./g.	4.36	4.99	4.82
(c) Salt Splitting Capacity, meq./g.	2.12	4.63	4.31
(d) Difference in Capacity, %	51.50	7.20	10.50
(e) Bulk Density, H Form, g.(dry)/ml.(wet)	0.27	0.36	—

(ii) 5g. of air-dried resin sample of Sindex-C26 was taken in four bottles and treated with 500 ml. chlorine water of varying concentration, viz. 104, 198.5, 390 and 730 ppm. as chlorine, respectively. The bottles were kept for a day with intermittent shaking. Solutions were then analysed residual chlorine and resin samples for capacity (Table 2).

Similar studies were made in almost analogous way with other oxidizing agents for both the ion-exchangers, viz. Sindex-C26 and Dowex-50W $\times$ 8. The oxidizing agents used were potassium permanganate and potassium dichromate. The capacities of the resins after treatment were determined (Table 3).

The estimation of chlorine, potassium dichromate and potassium permanganate were carried out iodometrically.

Results and Discussion

By treating the resin Sindex-C26 with 0.1 N chlorine water, it was observed that the resin granules were

converted from black to brownish red in colour indicating the formation of some chromophoric groups. Further, it had been observed that the residual liquid gave a positive test for sulphate which came out of the resin to solution phase.

By treating the resin Sindex-C26 with chlorine water 0.1N concentration or chlorine water of different concentrations ranging from 104 to 730 ppm, it was found that the strong acid capacity of the resin decreases but at the same time an increase in the total exchange capacity was observed. The swelling and moisture content have also increased in all the cases as is evident from Table 2, which gives a clear indication that the degree of cross linking was affected by treatment with chlorine. Further, it can be seen that the effect of the treatment of different chlorine concentrations studied were almost the same.

In case of the unfunctional sulphonated cation-exchange resin Dowex-50W $\times$ 8, a decrease in salt-splitting capacity was noted with no change in total capacity after treating with chlorine water of 0.1N

TABLE 2—CAPACITIES SINDEK-C26 AFTER TREATING WITH CHLORINE WATER OF DIFFERENT CONCENTRATIONS

Sl. No.	Concn. of Chlorine Water, ppm	Chlorine Reacted, meq./g.	S. S. C. meq./g.	T. e. c., meq./g.	Difference in Capacity, %	Bulk Density, g./ml.	Moisture Content, % w/w	Swelling, %
1.	0	0	2.23	3.93	43.20	0.36	45.8	57.1
2.	104.0	0.27	2.12	4.29	50.60	0.29	52.1	63.5
3.	198.5	0.48	2.12	4.32	51.04	0.26	52.1	63.5
4.	390.0	0.83	2.11	4.35	51.10	0.26	51.8	64.5
5.	730.0	1.24	2.12	4.34	51.20	0.27	55.9	65.6

TABLE 3—CAPACITIES OF SINDEK-C26 AND DOWEX-50W $\times$ 8 AFTER TREATMENT WITH DIFFERENT OXIDIZING AGENTS (Time of Contact: 144 hr)

Sl. No.	Resin Selected	Reagent	Reagent Reacted with Resin, meq./g.	Salt Splitting Capacity, meq./g.	Total Exchange Capacity, meq./g.	Percentage Difference in Capacity (5)-(4) $\times$ 100	Bulk Density, H ⁺ Form
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
1.	Sindex-C26	0.1N Dichromate in 0.6N H ₂ SO ₄	6.65	1.54	3.89	60.6	0.36
2.	-do-	0.05N Dichromate in 0.6N H ₂ SO ₄	3.63	1.73	3.90	55.9	0.35
3.	-do-	0.1N KMnO ₄ in 0.6N H ₂ SO ₄	9.62	2.20	4.49	50.0	0.28
4.	-do-	0.05N KMnO ₄ in 0.6N H ₂ SO ₄	3.40	2.24	4.73	52.0	0.31
5.	Dowex-50W $\times$ 8	0.1N Dichromate in 0.6N H ₂ SO ₄	1.96	3.84	5.19	35.1	0.38
6.	-do-	0.05N Dichromate in 0.6N H ₂ SO ₄	0.11	3.89	5.35	27.3	0.31
7.	-do-	0.1N KMnO ₄ in 0.6N H ₂ SO ₄	9.52	5.12	5.45	6.0	0.24
8.	-do-	0.05N KMnO ₄ in 0.6N H ₂ SO ₄	4.12	5.19	5.66	8.6	0.31

concentration. Almost similar inference can be drawn from the results of the earlier workers⁵.

In the case of Sindex-C26, the chlorinated resin produced particle swelling due to the weakening of its structure and particle break-down occurred resulting in a loss in capacity due to an increase in the soluble active material. But the sulphonated resin, Dowex-50W $\times$ 8, on exposure to chlorine tolerated a good proportion of it, and after complete bleaching, ceased to remove chlorine from the solution, so little change in its capacity was noted on chlorination.

The mechanism of formation of weak and strong acid groups for resins having phenolformaldehyde structure after treating it with chlorine has been given in details by Braithwaite *et al*². In the present study the actual mechanism was followed by path B of their mechanism as the weak acid capacity had increased with a decrease in strong acid capacity.

From Table 3, it can be seen that with potassium dichromate solution in sulphuric acid, more reagent reacted with Sindex-C26 than in the case of Dowex-50W $\times$ 8. The salt-splitting capacity for Sindex-C26 has decreased with almost no change in the total capacity, which showed that only sulphonic acid groups were being affected by it. It is further confirmed by the increase of sulphate ion in solution which came out of the resin nucleus. Similarly, Dowex-50W $\times$ 8 is also being affected by it as the strong acid capacity is reduced with very little change in total capacity.

In case of permanganate solution in sulphuric acid medium, the reagent reacted is almost same for both the resins. In salt-splitting capacity, no change was observed for Sindex-C26 but an increase was noted in its total capacity. Similar inference can be drawn from the results for Dowex-50W $\times$ 8 so permanganate had similar effects on both the resins. It showed that sulphonic acid groups are not affected but the weak acid groups are formed by oxidation, thereby increasing its total capacity.

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The zeta potential of Fuller's earth suspension of 100, 250, 500 and 1000 mg./l concentrations in natural surface water has been studied in presence of aluminium sulphate concentration of nil, 0.145×10^{-4} , 1.45×10^{-4} and 5.8×10^{-4} M at pH varying from 4 to 9. The effect of the ionic environment present in surface water on zeta potential has been compared with those obtained earlier with Fuller's earth suspensions in distilled water medium.

Industrial Application of Zeta Potential Studies: Effect of Aluminium Sulphate on Destabilization of Clay Suspensions in Surface Water Medium

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Introduction

Aluminium sulphate, commonly known as filter alum, is the most widely used coagulant for clarification of turbid water. Optimum destabilization of the suspended clay colloids is achieved at a point where zeta potential (ZP) is almost zero, i.e. near the isoelectric point (iep). It has been found in earlier studies¹ that during destabilization of clay suspensions in distilled water using aluminium sulphate and ferric sulphate coagulants, the iep shifts towards the acidic side with increase in the clay concentrations and towards the alkaline side with increase in the coagulant doses.

The present study had been carried out to measure the ZP of Fuller's earth (F.E.) suspended in surface water medium using aluminium sulphate as coagulant in order to determine the effect of the ionic environment present in the medium. The observations have been taken from nil to 5.8×10^{-4} M aluminium sulphate concentrations at four different levels of clay concentration, viz. 100, 250, 500 and 1000 mg./l., with pH varying from 4 to 9. These findings have been compared with the data obtained earlier¹ under similar conditions except that the medium of suspension was distilled water.

Experimental

Surface water, collected from the Damodar river near the fertilizer factory at Sindri during September

1972, was found to contain 460 mg./l suspended solids and its total alkalinity and total hardness were 36 and 50 respectively (expressed as mg./l. calcium carbonate). This water was centrifuged for 15 min. at 10,000 rpm, sufficient to remove completely the suspended matter. The supernatant was collected in a bulk quantity as stock water, at the time required for the present study.

The cation-exchange capacity (CEC) of the Fuller's earth, determined earlier¹ as 34, was used. F. E. stock suspension was prepared by adding about 10 g. of F. E. to 1 lit. of the stock water, allowing it to stand overnight for wetting, shaking the next morning, settling again for about 30 min, and then decanting the supernate to an 1 lit. flask. The concentration of the suspended solids in this stock suspension, determined gravimetrically, was found to be 1705 mg./l.

Reagent grade (BDH) aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$] was used. Its solution (29 mM) was prepared by dissolving 1.814 g. $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ in 100 ml. distilled water. Hydrochloric acid and sodium hydroxide of 0.1 N strength were used for pH adjustments. Philips battery-operated pH meter*, and a zetameter** were used for pH and ZP determinations respectively. Sorvall SS-3 centrifuge** was used for centrifugation.

*Model PRg401

**Supplied by Zetameter Inc., New York

ZP studies of F. E. suspensions had been carried out at concentrations 100, 250, 500 and 1000 mg./l. prepared by appropriate dilution of the stock suspension with stock water. Five 500 ml. samples of each concentration were taken successively and to this were added nil, 0.25, 1.0, 2.5 and 10.0 ml. of stock solution of aluminium sulphate, so that the final concentration would become nil, 0.145×10^{-4} , 0.58×10^{-4} , 1.45×10^{-4} and 5.8×10^{-4} M respectively. Afterwards, the pH of each suspension was lowered by adding acid to pH 4.0 and ZP was measured. Then, the pH of the same suspension was gradually raised to 9.0 by adding alkali and ZP was measured at different pH levels. All ZP values were average of 15-20 readings.

Results and Discussion

ZP values were plotted against pH. Figs. 1 to 4 represent the different concentrations, viz. 100, 250, 500

and 1000 mg./l, of F.E. suspensions with varying doses of aluminium sulphate. The initial ZP was about -10 to -15 mv with nil aluminium sulphate concentration. With 100 mg./l. clay concentration (Fig. 1), it was observed that 0.145×10^{-4} M aluminium sulphate concentration raised the ZP to zero at pH 6.0, while the other three higher concentrations, viz. 0.58×10^{-4} , 1.45×10^{-4} and 5.8×10^{-4} M, raised it to the positive side, which gradually decreased and became negative at higher pH. The curves for 250 and 500 mg./l. clay concentrations (Figs 2 and 3) are almost identical in nature indicating that the lowest aluminium sulphate concentration (0.145×10^{-4} M) could not raise the ZP to the positive side. The other three higher concentrations raised ZP to the positive side, which gradually decreased and became negative at higher pH. In case of 1000 mg./l. clay concentrations, the lowest aluminium sulphate concentration (0.145×10^{-4} M) could not raise

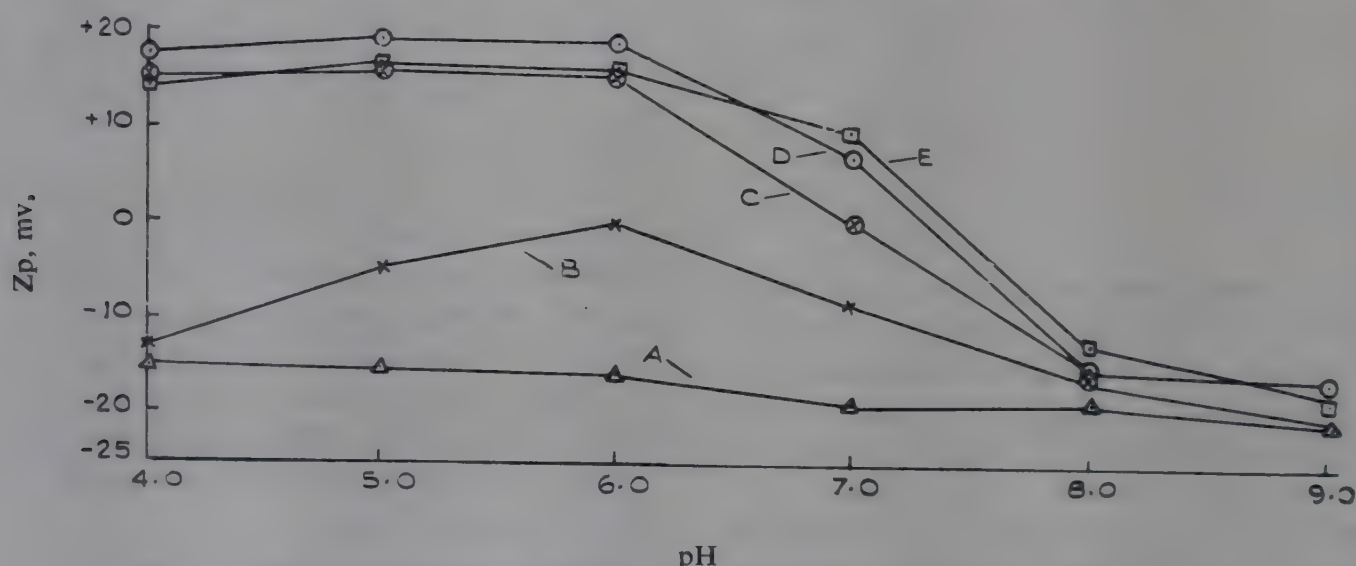


Fig. 1—Fuller's Earth Suspension in River Water Supernate = 100 mg./l.
 $\text{Al}_2(\text{SO}_4)_3$ Dose, moles/l.
 A nil
 B 0.45×10^{-4}
 C 0.58×10^{-4}
 D 1.45×10^{-4}
 E 5.8×10^{-4}

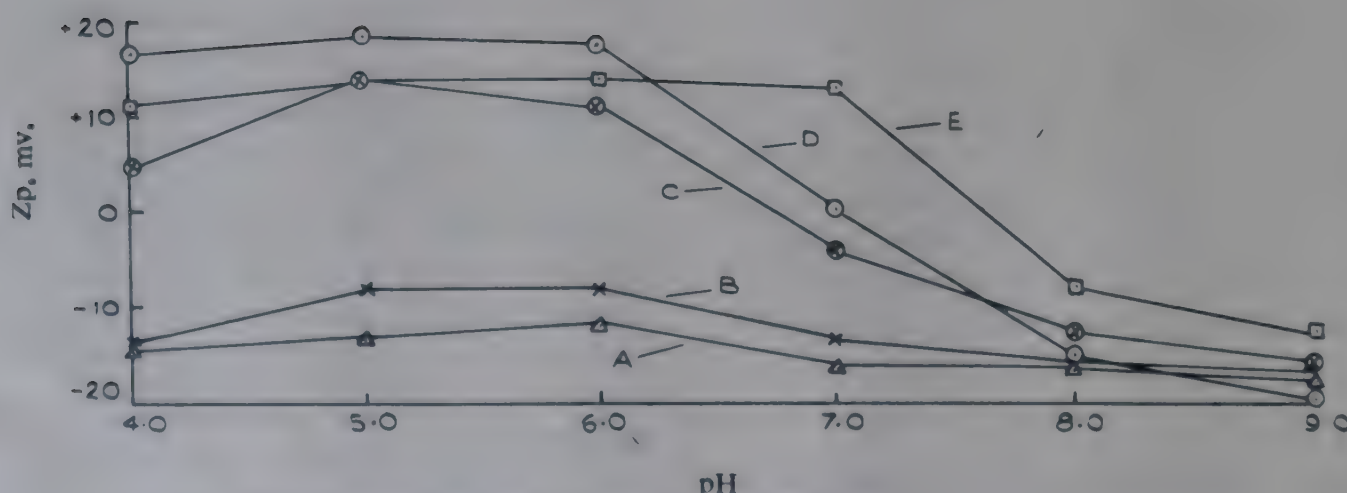


Fig. 2—Fuller's Earth Suspension in River Water Supernate = 250 mg./l.

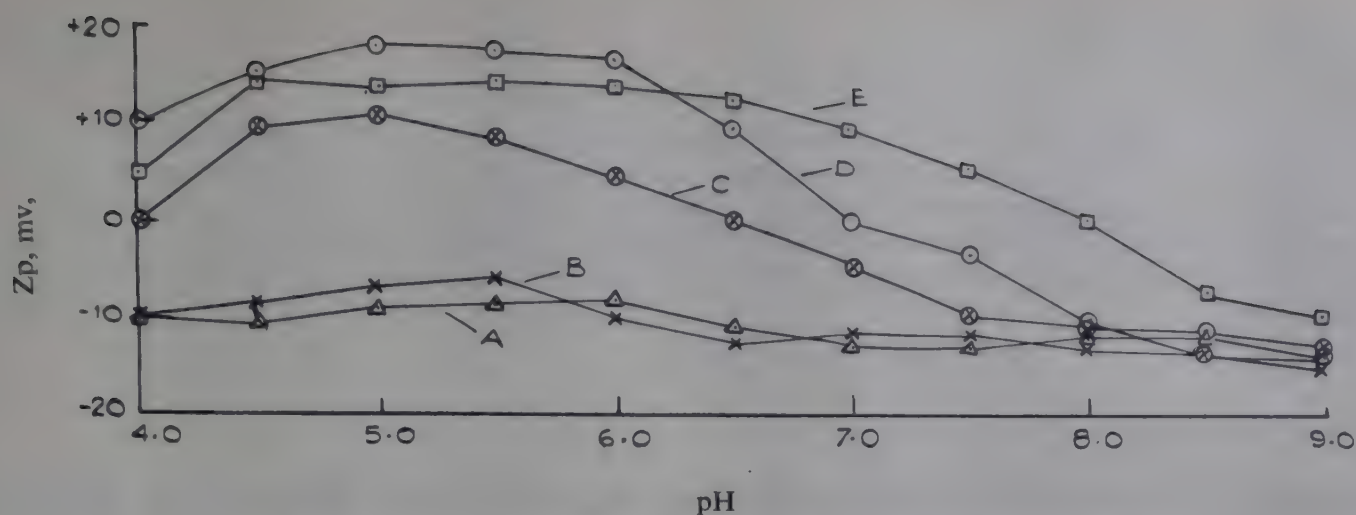


Fig. 3—Fuller's Earth Suspension in River Water Supernate = 500 mg./l.

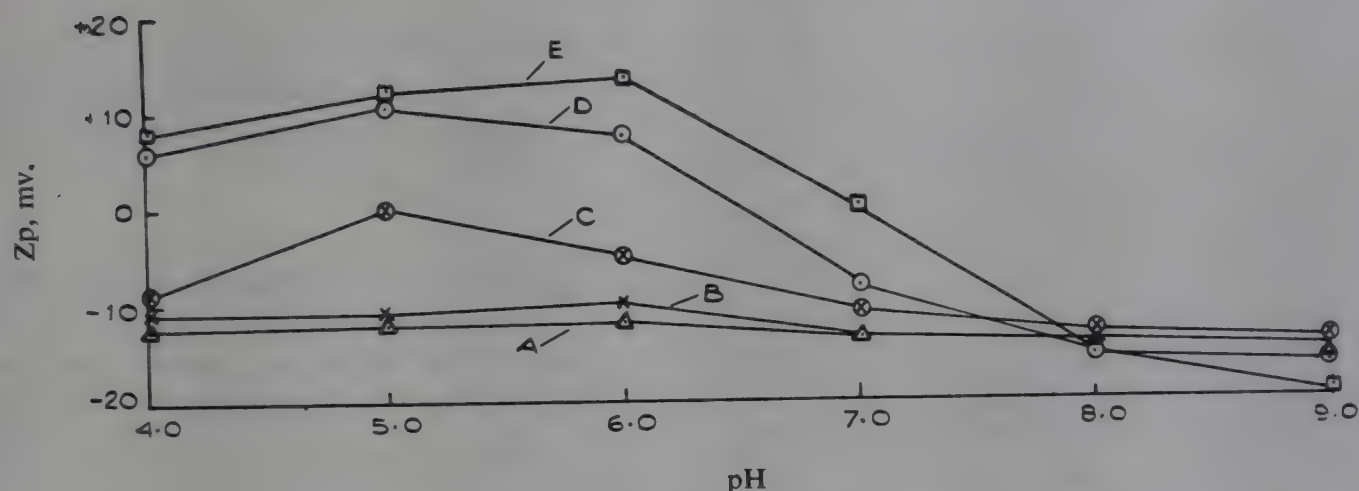


Fig. 4—Fuller's Earth Suspension in River Water Supernate = 1000 mg./l.

the ZP to the positive side. The next higher concentration, viz. 0.58×10^{-4} M, raised the ZP to zero at pH 5.0 and the two highest concentrations, viz. 1.45×10^{-4} M and 5.8×10^{-4} M, raised it to the positive side, which gradually decreased and became negative with the increasing pH.

The isoelectric points obtained are given in Table 1. The values within brackets were obtained earlier¹ from

TABLE 1—ISOELECTRIC POINTS OF SURFACE WATER SUSPENSIONS

Clay Concentration	$\text{Al}_2(\text{SO}_4)_3$ Concentration, moles/l.			
	0.145×10^{-4} M	0.58×10^{-4} M	1.45×10^{-4} M	5.8×10^{-4} M
100	6.0 (5.5)	7.0 (7.65)	7.3 (8.22)	7.44 (8.50)
250	=	6.72 (6.3)	7.0 (6.5)	7.6 (8.0)
500	=	6.5 (4.5)	7.0 (6.32)	8.0 (7.32)
1000	=	5.0 —	6.5 (5.5)	7.0 (7.0)

similar aluminium sulphate and F.E. concentrations in distilled water suspensions.

It can be seen that, in general, the iep values for suspensions in surface water medium (SWM) shifted towards the acidic side with increase in the clay concentration and to the alkaline side with increase in the alum concentration.

With 100 mg./l. clay concentration, higher iep values were obtained in SWM than in distilled water medium, only for the lowest alum concentration, whereas with 250 mg./l. clay concentration iep values for SWM were higher for all except the highest alum concentration. For 500 mg./l. and 1000 mg./l. clay concentrations iep values for SWM were higher than those in distilled water for all the alum doses.

Acknowledgement

The authors are thankful to the General Manager, P & D Division, for his interest in this work.

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[Original mss. received on July 11, 1974]

To evaluate the characteristics of the raw water of the *Brahmani* river near Talcher, where a 1500 tes day urea factory is being set up by the FCI Ltd. and which would draw its water requirement from this river, a year round survey of the river water was made. The quality of the water seems to be in the category of a soft to moderately hard water, with low dissolved solids and silica and free from any significant pollution. The only objectionable constituent in the water is high turbidity during the rainy monsoon months and as such clarification in a suitable clarifier is the primary treatment step required for such water.

Raw Water Characteristics of the *Brahmani* River at Talcher

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Introduction

The *Brahmani* is the second largest river of Orissa. It is formed after the confluence of two small rivers the *Sankha* and the *Koel* at Panposh near the steel town Rourkeala. The *Sankha* and the *Koel* have their origin

in the Plateau of Chotanagpur, Bihar. The combined flow of the *Sankha* and *Koel* hanceforth termed as the *Brahmani*, first flows southwardly, and ultimately in the eastern direction towards the Bay of Bengal. During this journey a good number of small tributaries also



Fig. 1, Course of River *Brahmani*

TABLE 1—ANALYSIS OF THE *Brahmani* RIVER WATER AT TALCHER (SHOWING RANGE OF VALUES IN mg./l. EXCEPT WHERE OTHERWISE STATED)

No.	Month of Collection	Temp., °C	pH	Free Carbon Dioxide as CO ₂	Dissolved Oxygen as O ₂	Alkalinity as CaCO ₃			Hardness		Chloride as Cl	Sulphate as SO ₄	Silica as SiO ₂	Total Iron as Fe	Sodium Alkalinity	Total Dissolved Solids	Turbidity
						P	M	Ca	Mg	Total							
1.	April 1970	31-32	8.2-8.4	0.5-1.0	7.4-9.0	0-3	80-98	41-48	33-38	74-86	6.0-7.75	4.6-13.1	12.0-14.3	0.05-0.07	6-12	110-140	40-110
2.	May 1970	30-32	7.0-7.3	8-12	—	0-0	78-94	46-53	27-32	73-85	5.0-6.8	3.5-6.8	12.8-14.1	0.02-0.09	4-9	108-130	10-33
3.	June 1970	29-34	6.8-8.3	0.5-7.0	6.0-7.2	0-3	33-78	14-46	9-25	23-71	1.3-5.0	1.8-3.5	9.4-12.6	0.03-0.18	7-10	72-110	200-3000
4.	July 1970	30-31	7.7-7.8	1.0-2.0	—	0-0	36-40	19-21	10-15	29-36	2.0-2.3	1.8-2.0	10.5-11.0	0.18-0.20	4-7	70-75	800-900
5.	August 1970	27-31.5	7.3-7.6	1.6-2.0	6.6-6.9	0-0	40-49	24-26	16-22	40-48	2.5-4.0	2.0-6.0	8.5-10.3	0.05-0.10	0-1	75-100	800-1200
6.	November 1970	22-26	8.0-8.1	1.0-2.0	8.0-9.0	0-0	72-74	36-38	25-26	61-64	4.5-6.0	3.0-4.0	7.5-9.0	0.02-0.02	9-10	95-104	10-20
7.	February 1971	22-29	7.9-8.1	1.0-2.5	8.1-8.3	0-0	73-80	43-46	21-28	64-74	4.0-5.0	8.0-9.6	10.0-10.3	0.04-0.04	6-9	100-118	10-20

join it. In the district of Dhenkanal (Orissa) it passes by Talcher, where a coal-based fertilizer factory with a rated capacity of 1500 te/day urea is being set up by the FCI Ltd. Further down near Cuttack, it meets the *Mahanadi*, the biggest river of Orissa. The sacred river, *Baitarani*, also joins it near Kendrapara. The course of the *Brahmani* is shown in Fig. 1.

As the proposed fertilizer factory at Talcher would draw its entire requirement of water (about 16.5 mgd) from the *Brahmani* river, it was felt necessary to evaluate the water characteristics of the *Brahmani* river near Talcher. With this view in mind, an year round survey of the characteristic of *Brahmani* river water was made. The period of survey was from April '70 to Feb. '71 covering all the important seasons of the year.

Procedure

Samples of raw water were collected periodically from a fixed sampling point near the existing State Govt.'s power plant pump house, and were analysed in our field laboratory specifically set for this purpose for pH, alkalinity (phenolphthalein and methyl orange), hardness (total and calcium), turbidity, dissolved carbon dioxide, dissolved oxygen, total iron and temperature. The rest of the analyses were done in the P & D Divisions' laboratory at Sindri, following the standard methods¹.

The results of the analysis monthwise (in range of values) are given in Table 1.

Discussion

From the chemical analysis (Table 1), the *Brahmani* river water at Talcher may be classified in the category of a soft to moderately hard water having zero non-carbonate hardness, and low in silica and sodium alkalinity and very low in chloride, sulphate and iron with moderate amount of turbidity, except in the rainy months of monsoon season, and is free from any significant pollution.

From the treatment point of view, it is a good type of water requiring only clarification in a conventional type of clariflocculator as the principal treatment step. The clarified water after chlorination or similar chemical disinfection may be used for potable or industrial process purposes. For boiler feed purpose also, this is a desirable quality of water as the dissolved solids and silica are quite low.

Acknowledgements

The authors gratefully acknowledge the fruitful guidance received from Sri B. K. Dutta and Sri G. S. Bhattacharyya during this study.

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Coal tar extract and formaldehyde alone and in combination were tried as inhibitor for carbon steel for scale removal system containing hydrochloric acid. The inhibitors gave good performance even in a bimetallic system of carbon steel and copper.

Inhibitors for Scale Removal System

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Introduction

For the chemical cleaning of carbon steel equipments in process industries, hydrochloric acid doped with inhibitors is commonly used for the removal of scale. A number of organic nitrogen compounds have been used as effective pickling inhibitors¹⁻⁵. But in the case of bimetallic systems, such as encountered in exchangers, etc., where the shell is of carbon steel and tubes of copper, chemical cleaning is difficult and is therefore normally done manually. In the present investigations, an extract prepared from coal tar and formaldehyde alone and in combination were used for inhibiting the

corrosion of carbon steel and carbon steel coupled to copper in hydrochloric acid and the results were compared with the commercially available product, Clean-sol.

Experimental

Rectangular test coupons of $6.2 \times 1.0 \times 0.2$ cm. size of carbon steel and copper were taken for experiment. The mild steel coupons uncoupled and those coupled with copper were kept immersed in the respective media for 6 hours at different temperatures. The weight-loss was recorded as mg./sq. dm./day. The concentrations of hydrochloric acid chosen were in the range

TABLE 1—INHIBITION OF CORROSION OF CARBON STEEL

Sl. No.	Inhibitor Concentration			Inhibition of Corrosion in Hydrochloric Acid, %							
	Tar Extract, % V/V	40% Formaldehyde, % V/V		Room Temperature		50°C		60°C		70°C	
				0.931 N	1.8621 N	0.931 N	1.8621 N	0.931 N	1.8621	0.931 N	1.8621 N
1.	—	—	Cleanzol	99.20	99.30	98.31	99.29	98.24	99.20	94.97	98.79
2.	1	—	—	99.77	99.22	99.33	99.11	99.18	98.58	98.27	97.59
3.	2	—	—	99.78	99.49	99.52	99.49	99.47	98.65	98.54	97.82
4.	3	—	—	99.79	99.51	99.72	99.50	99.66	98.95	98.92	98.13
5.	—	1	—	99.28	99.00	99.17	99.00	99.02	98.98	98.93	98.92
6.	—	2	—	99.40	99.31	99.37	99.26	99.23	99.14	98.97	98.97
7.	—	3	—	99.45	99.37	99.38	99.26	99.31	99.17	98.98	98.98
8.	1	2	—	99.84	99.72	99.79	99.66	99.66	99.63	99.63	99.60
9.	2	2	—	99.88	99.80	99.82	99.75	99.72	99.70	99.70	99.62
10.	2	4	—	99.90	99.84	99.88	99.83	99.74	99.70	99.72	99.67
11.	4	4	—	—	99.86	99.88	99.83	99.74	99.72	99.73	99.70

TABLE 2—INHIBITION OF CORROSION OF CARBON STEEL IN COUPLED SYSTEM OF CARBON STEEL AND COPPER

Sl. No.	Inhibitor Concentration		Inhibition of Corrosion in Hydrochloric Acid, %							
	Tar Extract, % V/V	40% Formaldehyde, % V/V	Room Temperature		50°C		60°C		70°C	
			0.931 N	1.8621 N	0.931 N	1.8621 N	0.931 N	1.8621 N	0.931 N	1.8621 N
1.	1	—	99.66	99.66	99.56	99.45	99.45	99.36	99.38	98.76
2.	2	—	99.70	99.70	99.66	99.47	99.47	99.43	99.20	98.90
3.	—	3	99.58	99.47	99.52	99.47	99.15	98.70	98.67	98.68
4.	2	4	99.78	99.63	99.75	99.61	99.62	99.59	99.60	99.58

normally used for pickling and scale removal. In each experiment, 400 ml. of solution was taken in a 500 ml. Erlenmeyer flask. The formaldehyde solution used was of analytical reagent grade.

The coal tar extract was prepared in the following way : 500 ml. of coke oven by-product tar was mixed with 1:1 hydrochloric acid and refluxed for 8 hours. The liquid portion was then drained off the bottom resinous portion washed with water and total volume made up to 500 ml. From this stock solution measured amounts were added.

Results and Discussion

The results of weight-loss experiments with carbon steel are presented in Table 1. The inhibition of corrosion in 0.931 N hydrochloric acid by 'Cleasol' was 99.2 per cent but it dropped to 94.97 per cent at 70°C, whereas with 3 per cent tar extract it was 98.92 per cent. The corresponding corrosion inhibition by 3 per cent formaldehyde (of 40 per cent sol.) was 98.98 per cent. It is further observed that a combination of tar extract and formaldehyde gives much improved protection than either of these used alone. The protection

provided by 2 per cent tar extract and 4 per cent formaldehyde was 99.72 per cent and 99.67 per cent at the hydrochloric acid concentrations of 0.931 and 1.862 N respectively.

In the coupled system of carbon steel and copper (Table 2), 2 per cent of tar extract and 4 per cent formaldehyde gave inhibition of 99.6 per cent and 99.58 per cent at the hydrochloric acid concentrations of 0.931 and 1.862 N respectively. The results clearly indicate that even in coupled system the efficiency of this combination has not decreased to a marked extent.

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In a fertilizer factory failure occurred of the tube and tube plate in the reformed gas waste heat boiler. The failure of the stainless steel ferrule appeared to have occurred due to carburization and oxidation and of carbon steel tube and tube plate due to subsequent overheating.

Failure of Waste Heat Boiler : A Case Study

By K. M. VERMA, H. GHOSH, S. C. VERMA,
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In a fertilizer factory failure occurred of the tube and tube plate in the reformed gas waste heat boiler. When the boiler was taken up for annual maintenance, leakage was observed during hydraulic testing at 7 kg./cm² pressure. On removal of the stainless steel plate the refractory lining was observed to have cracked. On removal of the refractory lining the mild steel tubes were found to have their ends broken at the junction with the tube sheet. The inside surface of the tube sheet hole along with the tubes were found burnt to a depth of 1/16". In the central area of the tube sheet the burning was excessive and the depth of burning was to the extent of 1/4". The stainless steel ferrules were also observed to have become very brittle and at places fused with the tubes.

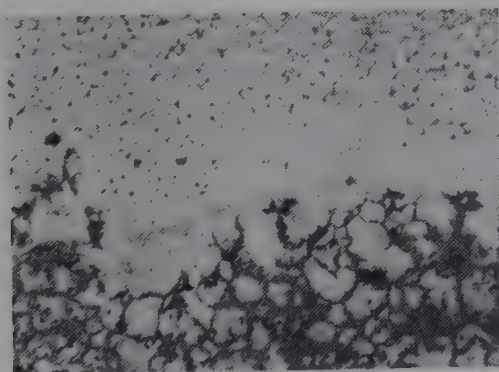


Fig 1—Inner Surface of the Failed Stainless Steel Ferrule
Showing Austenitic Structure with Presence of
Carburized and Oxidized Layer. x 120
[Reduced to half size]

The boiler is of shell and tube type with inserted tube plates and is inclined at 5° to the horizontal. The re-

formed gas enters at the raised end and passes through 183 tubes which have a total heating surface area of 72.5 m². The stainless steel ferrules protect the inlet ends of all tubes from the high gas temperature. The tube plate is protected by a refractory insulating material and a stainless steel plate. The working pressure of the boiler is 21 kg./cm². The material details and service conditions were as follows :

Tube —medium carbon steel 1½" OD×9 Swg
expanded and seal-welded.

Tube Sheet —Material to B.S. 1633 grade C

Ferrule —AISI 310 stainless steel

	Gas at inlet	Gas at outlet
Gas Temperature	876°C	370°C
Gas Pressure	16.73 kg./cm ² .	16.69 kg./cm ² .

Gas Composition, %

CO₂ 15.9, CO 8.0, H₂ 3.68, N₂ 18.91, A 0.34, CH₄ 0.17 and H₂O 53.0.

A close examination of the failed equipment revealed that the stainless steel ferrules and boiler tubes from the central region of the boiler were more affected than the peripheral tubes. The stainless steel ferrule appeared to have thinned down from the inside.

The analytical check-up showed that the materials of construction of the ferrule, tube and tube sheet were within manufactures' specification. A metallographic examination of the failed ferrule revealed the structure to be austenitic with carbide precipitation in and along the austenitic grain boundaries. Sigma phase was also

present. Both the inner and outer surfaces appeared carburized and oxidized (Figs. 1 and 2) the extent of which was more on the inner side. In the ferrules, the extent of carburization was more in the central regions than in the peripheral.



Fig. 2—Outer Surface of the Failed Stainless Steel Ferrule from the Central Region of the Boiler Showing Austenitic Structure with the Presence of Carburized and Oxidized Layer x 340
[Reduced to half size]

The metallographic structure of the mild steel boiler tubes was ferrite-pearlite. The failed boiler tubes in the

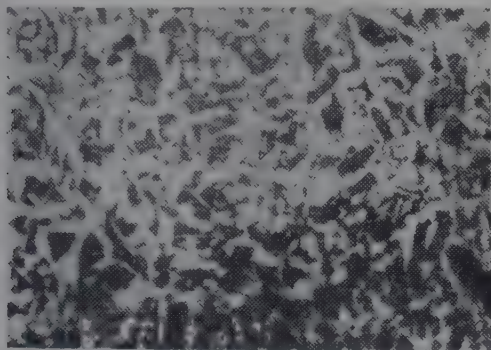


Fig. 3—Mild Steel Boiler Tube from the Peripheral Region Showing Ferrite—Pearlite Structure with Carburization of the Inner Surface, x 340
[Reduced to half size]

peripheral region showed carburization on the inner surface (Fig. 3), while the boiler tubes in the central region appeared to have suffered oxidation and overheating from both inner and outer surfaces. The central core appeared decarburized and the structure was only ferritic (Fig. 4).

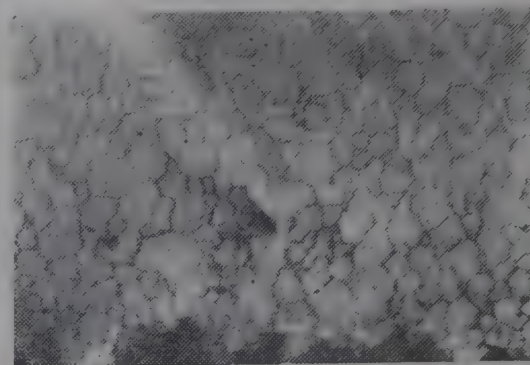


Fig. 4—Mild Steel Boiler Tube from the Central Region of the Boiler Showing Decarburization x 340
[Reduced to half size]

The failure of stainless steel ferrule appeared to have occurred because of carburization and oxidation. It has been reported that the carburized layer is brittle at lower temperatures, and may crack due to sudden shock. It is probable that due to abrupt cooling of the reformed gas at the place where boiler tubes are fitted into the tube plate, the carburized layer may crack and peel off due to thermal shock exposing fresh metal to the action of the gas. This intermittent carburization and peeling off might have resulted in thinning and ultimate rupture of the stainless steel ferrule. After the failure of the stainless steel ferrule, the mild steel tubes and tube plate appeared to have failed due to overheating. For such service, ceramic or incoloy 800 ferrules are reported to give an improved and better service.

[Original mss. received on Sept. 23, 1974]

A pot culture experiment on paddy with four water-regime treatments, viz. 50 per cent water-holding capacity and the same water-holding capacity supplemented with additional level of nutrients, continuous saturation and submergence, was conducted with acidic (pH 5.7), neutral (pH 6.8) and alkaline (pH 8.5) soils. Submergence and saturation produced significantly higher yield of grain, straw and number of tillers compared with the two other treatments. The higher yield in submerged and saturated soils was possibly due to the absence of soil moisture stress and increased availability of major plant nutrients especially nitrogen, phosphorus and potassium compared to soils at 50 per cent water-holding capacity. The growth and yield of paddy were found to be significantly higher in acidic soil than in neutral and alkaline soils at all the water regimes.

Water and Fertility Management in Paddy Soils*

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Rice grows better under submerged soil conditions due to the increased availability of plant nutrients as a result of reducing processes¹⁻³. However, the wet land culture of rice, during land preparation and keeping the soil under submergence thereafter, needs vast irrigation resources. This much-needed water could easily be diverted to other important crops if chemical simulation of some of the benefits of submergence is possible. It was, therefore, deemed necessary to know if submergence can be dispensed with the application of higher levels of nitrogen, phosphorus, potassium and iron, etc. under 50 per cent water-holding capacity of soil without sacrificing the yield of paddy.

Material and Methods

The experiment was conducted under controlled pot culture conditions at Sindri with acidic (pH 5.7) soil from Kanke (Ranchi), neutral (pH 6.8) soil from the Research Farm, Sindri and alkaline (pH 8.5) soil from Samastipur. The relevant chemical composition of these soils is presented in Table 1.

5 kg. sieved soil (2 mm.) was taken in each of 36 uniform earthen pots (25 cm. ht × 22 cm. diam.). The treatments were as follows: (1) soil at 50 per cent water-holding capacity; (2) soil at 50 per cent water-holding capacity with additional nutrients; (3) continuous

saturation with no standing water; (4) continuous submergence (5 cm. standing water).

All the treatments with three replications received a basal dressing of 100:80:80 kg./ha of N: P₂O₅:K₂O in the form of urea, single superphosphate and muriate of potash respectively. Apart from this, treatment no. 2 received an additional dose of 25:20:20 kg./ha. of N:P₂O₅:K₂O respectively plus 10 ppm solution of Fe²⁺ at the tillering and preflowering stages as top dressing. Fe²⁺ was applied in the form of iron EDTA. The maximum water-holding capacity of the soils under study was determined in the laboratory. The 50 per cent water-holding capacity of soils from Kanke, Sindri and Samastipur contained 17.5, 16.0 and 20.0 per cent moisture by weight respectively. For maintenance of soil moisture in treatment nos. 1 and 2 one additional pot of each soil without plant was kept at 50 per cent water-holding capacity. These three pots were weighed daily and the amount of water lost from each soil was added in the respective experimental pots. Uniform rice seedlings (20 days old, var. IR 8) were transplanted one in each pot and kept till harvesting. Observations of total number of tillers were recorded at the preflowering stage. Weight of dry matter and yield of grain was noted after harvesting.

Results and Discussion

Grain Yield: The mean values of grain yield due to the water regimes and soil types are presented in Table 2. The results clearly show that with increasing level of

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TABLE 1—CHEMICAL COMPOSITION OF THE SOILS

Sl. No.	Place	District	pH	Ec, m. mhos/cm.	Organic Carbon, %	Av. P ₂ O ₅ , kg./ha	C. E. C., m.e./100 g.	Free CaCO ₃ , %	Free Fe ₂ O ₃ , %
1.	Kanke	Ranchi	5.7	0.25	0.39	16.1	15.00	0.086	1.77
2.	Sindri	Dhanbad	6.8	0.20	0.40	29.0	12.72	—	—
3.	Samastipur	Samastipur	8.5	0.65	0.41	12.0	—	21.30	0.32

water from 50 per cent water-holding capacity to submergence, the mean yield values increased significantly. The highest mean yield (22 g.) obtained was due to submergence and the lowest (8.4 g) due to 50 per cent water-holding capacity without additional nutrients. 50 per cent water-holding capacity treatment with additional nutrients doubled the yield (16.5 g.) compared to without additional nutrients. However, saturation and submergence clearly produced significantly higher yields than 50 per cent water-holding capacity with or without supplemented by additional nutrients.

TABLE 2—YIELD OF GRAIN, g./pot

Sl. No.	Treatment	Acidic Soil	Neutral Soil	Alkaline Soil	Mean
1.	50+ W. H. C	11.4	7.0	6.9	8.4
2.	50+ W. H. C+ additional nutrients	20.1	14.4	15.1	16.5
3.	Saturation	26.9	18.3	15.4	20.2
4.	Submergence	25.9	19.9	20.3	22.0
Mean		21.1	14.9	14.4	—
C. D. for treatment means		= 1.76 at 5% level.			
C. D. for soil means		= 1.53 -do-			
C. D. for soil × treatments		= 3.05 -do- (NS).			

The data also indicate that acidic soil recorded significantly higher yield of paddy at all the water regimes as compared to neutral and alkaline soils. Paddy yield produced by neutral and alkaline soils was at par at all the water regimes, except under saturation where it was markedly higher in neutral than alkaline soil. Neutral and alkaline soils recorded higher yields under submergence than saturation. On the contrary, acidic soils yielded higher at saturation (26.9 g.) compared to submergence (25.9 g.) but no significant difference was discernible between the yield values.

The interaction between the treatments and the soils for grain yield was found non-significant.

Straw Yield: The mean values of dry matter due to water regimes and soil types are shown in Table 3. The

data clearly show an increasing trend in the yield of straw with increasing level of water in the soils. The lowest yield of straw (10.6 g.) was noted in 50 per cent water holding capacity treatment without additional nutrients and the highest yield (27.7 g.) obtained was again due to submergence. While 50 per cent water-holding capacity treatment supplemented with additional nutrients yielded significantly higher amount (22.9 g.) of straw over the same treatment without additional nutrients (10.6 g.), it produced significantly lower straw than submergence (27.7 g.). However, no significant differences in straw yield were discernible between 50 per cent water-holding capacity with additional nutrients and saturation on the one hand and saturation and submergence on the other.

TABLE 3—YIELD OF STRAW, g./pot

Sl. No.	Treatment	Acidic Soil	Neutral Soil	Alkaline Soil	Mean
1.	50% W. H. C.	14.4	8.2	9.2	10.6
2.	50% W. H. C.+ additional nutrients	32.9	16.8	19.0	22.9
3.	Saturation	29.5	27.2	20.9	25.8
4.	Submergence	36.6	22.2	24.5	27.7
Mean		28.4	18.6	18.4	—
C. D. for treatment means		= 3.51 at 5% level			
C. D. for soil means		= 3.02 -do-			
C. D. for soil × treatment		= 6.07 -do-			

Under soil types, acidic soil again yielded significantly higher mean yield of straw (28.4 g.) as compared to both neutral (18.6 g.) and alkaline (18.4 g.) soils, the latter two soils being at par. While in acidic and alkaline soils submergence was found to give highest yield of dry matter than other treatments, in neutral soil the same was true with saturation.

There was a significant interaction between water regimes and soils in producing the dry matter of the plant.

Number of Tillers : The results of number of tillers according to treatments and soil types are given in Table 4. The trend in the mean values of tiller number due to water regimes and soil types is similar to that of grain and straw yield. Submergence and saturation produced 12.9 and 12.8 tillers respectively which were at par but significantly higher compared to 50 per cent water-holding capacity treatment with or without supplemented by higher levels of nutrients.

TABLE 4—NUMBER OF TILLERS PER POT

Sl. No.	Treatment	Acidic Soil	Neutral Soil	Alkaline Soil	Mean
1.	50% W. H. C.	6.6	3.3	3.6	4.5
2.	50% W. H. C. + additional nutrients	12.6	9.3	7.6	9.8
3.	Saturation	15.0	13.6	10.0	12.8
4.	Submergence	15.3	12.3	11.3	12.9
Mean		12.4	9.6	8.1	—
C. D. for treatment means		= 1.40 at 5% level			
C. D. for soil means		= 1.21 -do-			
C. D. for soil × treatments		= 2.42 -do-			

Among the soils again, significantly higher number of tillers were noted in acidic (12.4) compared to both neutral (9.6) and alkaline (8.1) soils. The interaction between soils and treatments for a number of tillers was non-significant.

The data of the present experiment clearly point out that submergence gives significantly superior growth and yield of rice. In controlled glass house conditions, saturation was at par with submergence in the acidic and neutral soils but inferior in alkaline soils.

50 per cent water-holding capacity treatment with additional nutrients in all the soils produced twice the

amount of yield as compared to without additional nutrients but it yielded significantly inferior compared to saturation and submergence. The better growth and yield of rice in flooded soils is apparently caused by factors (associated with excess water or anaerobic conditions) operating in the reproductive phase⁴. It has been suggested that the main retarding factors in soils at field capacity are the iron deficiency on neutral and alkaline soils and manganese and aluminium toxicity on acid soils fertilized with ammonium sulphate⁵. Naphade and Ghildyal³ also reported a significantly higher uptake of N, P and Fe in grain and straw under submergence and that of Mn under field capacity in an acid laterite soil and that a balanced uptake of Fe and Mn by the plant was necessary for higher rice yields. It is interesting to note that the $Mn^{3+} \rightleftharpoons Mn^{+2}$ system was dominant compared to $Fe^{3+} \rightleftharpoons Fe^{2+}$ system in the soils under study⁶⁻⁷. However, no visible symptoms of either iron deficiency or manganese toxicity were noticeable in the plants of the present studies.

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Rhizosphere, non-rhizosphere and rhizoplane fungal flora of *Phaseolus radiatus* L. at preflowering, flowering and post-flowering stages have been investigated. Out of 45 fungal species 9 were distributed in all the three environments, whereas 13 were distributed only in two environments. Other fungal forms were of restricted occurrence. Only a few were of dominant occurrence. The number of species was higher in rhizosphere region and least in rhizoplane. Quantitatively also the rhizosphere fungal flora was always higher. In rhizosphere region the fungal population was maximum at the time of flowering, whereas in non-rhizosphere the fungal population decreased gradually. Higher root leakage in flowering stage probably resulted in maximum fungi in the rhizosphere region.

Variation in Fungal Flora of Root Regions of *Phaseolus Radiatus* L.

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INTRODUCTION

The fungi present in the rhizosphere of leguminous plants have been studied extensively¹⁻⁴. The rhizosphere effect is more pronounced in the plants of this family due to the presence of root nodules²⁻⁵. It has been advocated that different plant species harbour some what specific micro-organisms in their rhizosphere⁶⁻⁸.

The changes in root exudation and soil composition with varying plant species and age have been widely reported. *Phaseolus radiatus* L., an important rainy season crop of northern India, has been selected to investigate the rhizosphere and rhizoplane mycoflora in relation to its different age.

Materials and Methods

The plants growing luxuriantly in a neighbouring field were selected for the present study. The intact roots of *P. radiatus* were aseptically collected in pre-flowering (Aug. 6, 1973), flowering (Sept. 5, 1973) and postflowering (Oct. 5, 1973) stages. Simultaneously, soil samples away from the root influence were also obtained for nonrhizosphere studies. The rhizosphere, rhizoplane and nonrhizosphere mycoflora of the above samples were examined by dilution plate method⁹. The modified Martin's medium was used in all the cases and fungal count was done after 6 days' incubation at $26 \pm 1^\circ\text{C}$.

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Results

45 species were isolated from the three environments, i.e. rhizosphere, rhizoplane and nonrhizosphere. 9 species were present in all the three environments, 7 species were present in both rhizosphere and nonrhizosphere, similarly 3 species of rhizoplane were also present in nonrhizosphere region. Three species were common in rhizosphere and rhizoplane regions. Besides these fungi, other forms were of restricted occurrence (Table 1).

5, 4 and 4 species were found to be dominant in the nonrhizosphere, rhizosphere and rhizoplane regions respectively. The species dominant in rhizosphere and rhizoplane were also isolated from non-rhizosphere, on the other hand, all the dominant species of nonrhizosphere region were not always present in rhizosphere and rhizoplane (Table 1).

TABLE 2—NUMBER OF SPECIES AND FUNGI/G DRY SOIL AT DIFFERENT SAMPLING PERIODS IN RHIZOSPHERE, NONRHIZOSPHERE AND RHIZOPLANE (Only number of species)

Sampling Period	Number of Species			Fungi/g dry soil	
	RS	RP	NR	RS	NR
Preflowering (Aug 6, 1973)	19	8	16	34296	17436
Flowering (Sept 5, 1973)	21	10	12	59530	14600
Postflowering (Oct 5, 1973)	24	13	12	36846	13396

RS=Rhizosphere

RP=Rhizoplane

NR=Nonrhizosphere

32, 16 and 28 fungal forms were isolated from rhizosphere, rhizoplane and nonrhizosphere regions respectively (Table 1). A glance at Table 2 indicates that fungal population in rhizosphere was least in preflowering stage reached to its highest peak in flowering condition and decreased subsequently. The trend was different in nonrhizosphere soil and the fungal population in this case decreased gradually (Table 2). The number of fungal species associated with rhizosphere and rhizoplane regions increased gradually from pre-flowering to postflowering stages. In nonrhizosphere region the trend was just the reverse.

Discussion

The number of fungal species isolated were least in the rhizoplane region and highest in the rhizosphere. The higher counts from the rhizosphere region is probably due to liberation of wide range of metabolites (root exudates) by the actively growing roots during their normal metabolism. Of the various constituents of root exudates, amino acids, sugars and organic acids play a major role in determining the mycoflora of a rhizosphere⁹. Besides these, the soil surrounding the root surface also influences the rhizosphere population.

The rhizosphere population was low in the beginning, increased subsequently and attained the highest peak at the time of flowering. The maximum root exudation which is predominantly responsible for the rhizosphere population is expected during this period¹⁰⁻¹¹. When the plants attained maturity they released maximum root leakage and the stage coincided with the maximum fungal (Table 2). Later, in post flowering stage the root exudation probably decreased and root tissues played the dominant role in governing the rhizosphere fungi¹¹. During this period the specific nature of the substrate limited the number of fungi in the rhizosphere. The lesser number of fungi in the rhizoplane may also be explained in the light of substrate specificity. The population in the nonrhizosphere region behaved differently and decrease in later stages may be accounted to the decreased food supply during the period. Other workers^{8,12,13}, have also observed similar variation in the mycoflora of the different regions.

Conclusion

Rhizosphere, nonrhizosphere and rhizoplane fungal flora of *Phaseolus radiatus* L. at preflowering, flowering and postflowering stages have been investigated. The

TABLE 1—DISTRIBUTION OF DIFFERENT FUNGAL SPECIES IN RHIZOSPHERE (RS), RHIZOPLANE (RP) AND NONRHIZOSPHERE (NR)

Fungi	Environment			Fungi	Environment		
<i>Absidia heterospora</i>	RS	RP		<i>P. humicola</i>	RS	NR	
<i>Rhizopus nigricans</i>	RS	RP		<i>Pachybasium</i> sp.	RS	NR*	
<i>Mucor hiemalis</i>	RS*	RP*	NR	<i>Acrophialophora fusispora</i>		NR*	
<i>Cunninghamella elegans</i>	RS			<i>Paecilomyces varioti</i>	RS		
<i>Syncephalastrum racemosum</i>		RP		<i>Humicola grisea</i>	RS	NR	
<i>Chaetomium</i> sp			NR	<i>Memnoniella echinata</i>		NR	
<i>Phoma hibernica</i>	RS			<i>Cladosporium herbarum</i>	RS		
<i>Monilia sitophila</i>			NR	<i>Curvularia tetramera</i>		RP	NR
<i>Trichoderma viride</i>	RS	RP	NR	<i>C. lunata</i>	RS	RP	NR
<i>Aspergillus fumigatus</i>		RP	NR	<i>C. pallescens</i>	RS*	RP	NR
<i>A. nidulans</i>	RS		NR	<i>Helminthosporium sativum</i>	RS		
<i>A. sydowi</i>	RS			<i>Tetracocco sporium paxianum</i>	RS		
<i>A. versicolor</i>	RS			<i>Alternaria humicola</i>	RS		
<i>A. flavus</i>	RS	RP	NR	<i>Chaetophoma confluens</i>			NR
<i>A. terreus</i>	RS	RP	NR*	<i>Fusarium nivale</i>	RS		
<i>A. flavipes</i>			NR	<i>F. oxysporum</i>		RP*	NR
<i>A. ustus</i>	RS			<i>Fusarium</i> sp.	RS		
<i>A. niger</i>	RS*	RP*	NR*	<i>Myrothecium roridum</i>	RS		NR
<i>A. candidus</i>			NR	<i>Epicoccum nigrum</i>			NR
<i>A. ochraceus</i>			NR	White sterile colony	RS		NR*
<i>A. aculeatus</i>	RS	RP	NR	Red sterile colony	RS	RP	
<i>Penicillium chrysogenum</i>	RS*	RP*	NR	Black sterile colony	RS		NR
<i>P. notatum</i>	RS						

* Dominant

number of species was higher in rhizosphere region and the least in rhizoplane. Quantitatively also the rhizosphere fungal flora was always higher. The flowering stage harboured maximum fungi in rhizosphere region whereas the population was higher in preflowering stage in nonrhizosphere region. Higher root leakage in flowering stage probably resulted to maximum fungi in rhizosphere.

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The effect of soil application of three different NPK fertilizers (each with three different concentrations) on the rhizosphere mycoflora of soyabean was studied by the method of Timomin using the modified Martin's medium. The number of species, total colony count and colony count/g. of dry rhizosphere soil decreased significantly in all the fertilized rhizospheres in contrast with their control counterparts. The species composition of the control and fertilizer rhizospheres differed to a great extent. The fertilizers showed their selective influence in establishing the specific rhizosphere mycoflora of their own. The effect of different treatments, however, was not significant.

On Myco-organic Component of Soyabean Rhizosphere

Part 1—Rhizosphere Fungi as Influenced by Soil Application of Some NPK Fertilizers

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Introduction

As may be expected, the quality and quantity of the microorganisms in the root region of plants are influenced by various factors, like nature and age (stage of growth) of the plant, type, moisture content, reaction and agricultural practices. The rhizosphere microflora as influenced by various agricultural practices has been studied by Clark¹, Clark and Thom², Katznelson *et al.*³, Lochhead⁴ and Venkatesan and Rangaswami⁵. The application of nutrients through commercial fertilizers should not only result in a better yield but also change the microflora of the root regions of the plants. The rhizosphere fungi as influenced by fertilizer application, has however received little attention⁶.

In this communication, an attempt has been made to interpret the observations on the relative effectiveness of soil application of NPK fertilizer-8:8:8; Suphala-15:15:15 and Suphala-20:20:0 on the rhizosphere microfungi of soyabean.

Materials and Method

Soyabean seeds (var. Punjab type 1) were obtained from U.P. Institute of Agricultural Sciences, Kanpur. For sowing, 100 earthenware pots were filled with 3 parts of sandy loam soil and one part compost, then

thoroughly mixed. Almost all the seeds germinated on July 15, 1973. The solutions of 1.25, 2.50 and 5.00 per cent of NPK fertilizer 8:8:8 (urea: ammonium phosphate:potash); 0.65, 1.30 and 2.60 per cent of Suphala [15:15:15 (ammonium nitrate: phosphate: potash)]; and 0.50, 1.00 and 2.00 per cent of Suphala 20:20:0 (ammonium nitrate:phosphate) were prepared by dissolving them in redistilled water. In the first treatment, 10 ml. of the solutions of these concentrations of all the fertilizer mixtures in question were applied on the surface of the pot-soil having 4-5 leaves, 3 weeks old single seedling per pot. The three successive applications of the same chemicals with the same concentrations but double in volume, i.e. 20 ml. plant/pot were made to the same plant in the same manner at 10 days intervals. The control plants were treated with the same volume of redistilled water. Ten plants of each treatment were randomly distributed under natural conditions in the College botanic gardens.

The samples were collected after 55 days' sowing. In all the cases, whether treated or control, the plants were carefully removed from the pot and the adherent soil was gently broken to release the root system which was then shaken to remove superfluous soil and immersed in 250 ml. of sterile distilled water contained in 500 ml. flasks. After a thorough shaking, the suitable dilutions were prepared, the roots removed and washed, the washings being collected in the original dilution

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flask. The suspensions were transferred to *petri* dishes (5 *petri* plates in each case) containing modified Martin's medium⁷. The plates were inverted and incubated for a week at room temperature (22±5°C). The fungi appearing on the nutrient plates were examined and identified. The data on the total number of fungal species associated with a particular rhizosphere, the total colony count and percentage occurrence of fungal species in different rhizosphere were recorded. The moisture in the original (soil water suspension) flasks were driven off and the contents weighed to compute the colony count/g. of oven dry rhizosphere soil. The allowance was made for the amount of material removed during dilutions.

Results and Discussion

It can be gathered from Table 1 that some fungi, viz. *Acrophialophora fusispora*, *Aspergillus flavus*, *A. niger*, *A. terreus*, *Curvularia geniculata* and *Fusarium oxysporum*, made their appearance in the rhizosphere from control as well as fertilized soils. *Chaetomium globosum*, was present in all the rhizospheres except for the (soils) fertilized with 1.00 and 2.00 per cent solutions of Suphala -20:20:0. Apart from the common

association of these forms with rhizospheres, selective adaptation of some species to a rhizosphere-treated with a particular type of fertilizer was remarkable. *Aspergillus carbonarius*, *A. flavipes*, *Penicillium stipitatum* and white and black sterile mycelia were found associated with rhizosphere of control and that treated with NPK fertilizer 8:8:8. *Fusarium chlamydosporum* apart from its association with control rhizosphere appeared in the rhizosphere from the soil fertilized with Suphala-15:15:15 and Suphala-20:20:0. *Mucor hiemalis* was still peculiar in its distribution. It appeared in the rhizosphere soil treated with NPK fertilizer 8:8:8 and Suphala-20:20:0. A few species, like *Aspergillus sydowi*, *Chaetomella rafigera*, *Cunninghamella echinulata* *Fusarium moniliforme* and *Rhizopus arrhizus*, were never found associated with unfertilized rhizospheres but appeared in the fertilized rhizospheres only. *Penicillium oxalicum* and *Thielavia sepedonium* were always confined to the rhizosphere from unfertilized soils and could never be encountered in the rhizosphere from fertilized ones. Thus, there is a marked variation in the species composition of different rhizospheres. This is attributable to the specificity of the effects imparted by different types of fertilizers. Although many quanti-

TABLE 1—OCCURRENCE OF FUNGI IN THE RHIZOSPHERE OF SOYABEAN (CONTROL AND TREATED WITH DIFFERENT CONCENTRATIONS OF NPK FERTILIZER 8:8:8 SUPHALA 15:15:15 AND SUPHALA 20:20:0)

Fungal Species	Control	Occurrence in Different Rhizospheres, %								
		NPK 8:8:8			Suphala 15:15:15			Suphala 20:20:0		
		1.25%	2.50%	5.00%	0.65%	1.30%	260%	0.50%	1.00%	2.00%
<i>Acrophialophora fusispora</i>	20.4	16.2	16.0	15.8	16.7	18.8	17.3	17.2	18.8	12.0
<i>Aspergillus carbonarius</i>	4.2	2.1	3.4	1.0	—	—	—	—	—	—
<i>A. flavipes</i>	2.0	1.6	1.5	1.0	—	—	—	—	—	—
<i>A. flavus</i>	15.5	8.3	8.0	7.5	11.4	14.8	12.6	11.1	10.1	10.5
<i>A. niger</i>	10.6	2.5	2.0	1.1	8.1	8.9	6.6	2.3	2.3	2.6
<i>A. sydowi</i>	—	—	—	—	—	—	—	8.7	18.2	30.3
<i>A. terreus</i>	10.0	6.3	4.8	4.7	3.0	3.9	2.3	6.3	6.1	3.3
<i>Chaetomium globosum</i>	7.2	4.6	2.1	2.0	4.5	4.5	4.5	4.5	—	—
<i>Chaetomella rafigera</i>	—	15.6	10.0	4.2	10.0	8.8	4.1	—	—	—
<i>Cunninghamella echinulata</i>	—	—	—	—	—	—	—	10.2	5.9	4.6
<i>Curvularia geniculata</i>	12.0	11.8	10.2	10.3	11.5	5.9	6.0	8.2	5.3	4.3
<i>Fusarium moniliforme</i>	—	1.6	1.5	1.2	10.6	5.9	5.9	3.6	—	—
<i>F. oxysporum</i>	2.6	4.7	3.8	3.8	4.2	3.9	3.0	3.0	2.1	1.2
<i>F. Chlamydosporum</i>	4.9	—	—	—	2.9	12.5	23.1	12.1	16.8	10.8
<i>Mucor hiemalis</i>	1.1	1.0	4.0	4.4	—	—	—	1.0	8.7	10.1
<i>Penicillium stipitatum</i>	2.8	1.6	1.4	1.2	—	—	—	—	—	—
<i>P. oxalicum</i>	1.1	—	—	—	—	—	—	—	—	—
<i>Rhizopus arrhizus</i>	—	—	—	—	17.8	11.7	13.6	13.6	10.3	11.1
<i>Thielavia sepedonium</i>	1.0	—	—	—	—	—	—	—	—	—
White sterile colony	2.1	10.3	12.8	18.1	—	—	—	—	—	—
Black sterile colony	3.5	13.8	28.8	27.0	—	—	—	—	—	—

tative studies of the fungi in the plant rhizosphere, as influenced by the agricultural practices, have been made yet very little is known about the effect of fertilizers on the quality of rhizosphere mycopopulation. The findings of the present investigation confirm the reports of Thom and Humfeld⁸ who noted that corn roots in the acid soils yielded predominating *Trichoderma* colonies whereas roots from alkaline soil seemed to be associated chiefly with *Penicillia* of biverticillate series. It has also been reported that the application of fertilizers to the soil has a direct influence on the microbial population and this effect varies with the type of manure added.⁹⁻¹² A marked variation is evident from the data (Table 1) and the variation observed confirm the above-noted reports.

It is also clear that the percentage occurrence of fungi was always higher in the rhizospheres of unfertilized soils than fertilized ones. This observation confirms the findings of Bagyaraj and Rangaswami⁶ who noted a marked decrease in the rhizosphere mycopopulation by the application of fertilizers. In the present study, the degree of decrease in the mycopopulation of rhizosphere of treated soil varied with difference of NPK mixtures. This agrees with the reports of Venkateswan¹³ who noted more decrease in the rhizosphere microflora due to the application of ammonium sulphate than due to others. There is no

significant difference in the total number of species isolated from the control and treated rhizosphere soils. The total colony count and colony count/g. of dry soil differed significantly.

Conclusion

An investigation on the rhizosphere microfungi of soyabean as influenced by the soil application of different doses of NPK fertilizer 8:8:8 (urea : ammonium phosphate:potash); Suphala 15:15:15 (ammonium nitrate:phosphate:potash) and Suphala 20:20:0 ammonium nitrate:potash) was undertaken. The application of fertilizers was found to decrease the quantity of rhizosphere fungal population significantly. The difference in the total number of species isolated was not marked. The species composition of the control and fertilized soils differed to a great extent. The fertilizers showed their selective influence in establishing the rhizosphere mycoflora. The effect of treatments was insignificant.

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TABLE 2—TOTAL NUMBER OF FUNGAL SPECIES ISOLATED FROM DIFFERENT RHIZOSPHERE, TOTAL COLONY COUNT AND COLONY COUNT/g. DRY RHIZOSPHERE SOIL

Factors	Different Rhizospheres									
	Control	NPK Fertilizer 8:8:8			Suphala 15:15:15:			Suphala 20:20:0		
		1.28 %	2.50 %	5.00 %	0.65 %	1.30 %	2.60 %	50 %	1.00 %	2.00 %
No. of Species Isolated	16	14	15	15	12	11	11	13	11	11
Total Colony Count	139	120	100	75	105	76	67	98	73	69
Colony Count/g. dry soil	3.3×10^5	2.3×10^5	7×10^4	8.5×10^4	2.1×10^5	2×10^5	8.3×10^4	2.2×10^5	1.1×10^5	8.1×10^4

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A modified sulphur burner has been used to estimate chlorine in monochlorobenzene, *o*-dichlorobenzene, *p*-dichlorobenzene, chloroform, carbon tetrachloride and DDT by combustion with ethanol and absorbing the products in the acidified silver nitrate solution. Except DDT, all the other compounds could be estimated by this method with fairly good accuracy. In the case of DDT, out of the five chlorine atoms only the aromatic substituted two chlorine atoms respond to this estimation.

Estimation of Organic Chlorine by a Combustion Method*

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Introduction

The analysis of organic chloro-compounds, having at least 5 per cent of the halogen, by combustion method is known to be the most reliable procedure for milligram-scale work and this is also known as a rapid analytical procedure¹. The organic chloro-compounds yield a mixture of free chlorine and hydrogen chloride after the combustion. The use of silver iodate amplifies chloride indirectly and evolves iodine six times the amount of chloride produced by combustion², while for the compounds having large percentages of chlorine, the use of sodium bisulphite is preferred, provided the excess is destroyed by oxidation with hydrogen peroxide¹. In this work, an acidified silver nitrate solution has been used. The method has been verified

by estimating the chlorine contents in a number of aliphatic and aromatic compounds—solid and liquid.

Experimental and Results

A sulphur burner (ASTM type) used for combustion was modified by incorporating a gas-washing bottle as the second absorber. Pure ethanol free from chloride was used in the lamp either to dissolve or dilute the chloro-compound and to ensure a smokeless combustion. The rate of burning of the fuel was controlled to about 5 g./hr with the help of a jet water suction pump. The absorbers were wrapped with carbon paper to avoid decomposition of the silver nitrate in the light. Measured volumes of the silver nitrate solution (10 per cent w/v) containing 2 per cent nitric acid was

TABLE 1—ANALYSIS OF ORGANIC CHLOROCOMPOUNDS

Compound	Formula	Chlorine Percentage		Per cent Error	Chloro-Compound: Ethanol
		Theoretical	Found		
Mono-chloro-benzene	C_6H_5Cl	31.525	31.200	—1.03	1:10
<i>o</i> -dichloro-benzene	$C_6H_4Cl_2$	48.264	47.907	—0.74	1:20
<i>p</i> -dichloro-benzene	$C_6H_4Cl_2$	48.264	47.540	—1.50	1:10
Chloroform	$CHCl_3$	89.108	89.790	0.77	1:10
Carbon tetrachloride	CCl_4	92.198	92.750	0.60	1:10
D. D. T.	$[(C_6H_4Cl)_2 CHCCl_3]$	50.035	20.229	—59.57	1:10
—do—	"	"	20.014	—60.00	1:20
—do—	"	"	19.514	—60.99	1:40

* This work was carried out in Durgapur Chemicals Ltd., Durgapur-8, West Bengal.

taken in the absorbers. After the combustion, the excess silver nitrate was estimated with standard ammonium thiocyanate solution using ferric alum as the indicator. The analyses of some chlorinated hydrocarbons are given in Table 1.

The analytical data (Table 1) show that the combustion method, using 1:10 and 1:20 mixtures of chloro-compounds and ethanol, is suitable for chlorine estimation in the aliphatic and aromatic compounds. A very interesting observation has been made on DDT, which showed that all the five chlorine atoms did not respond to this method. The average percentage of error from three sets of ignition mixture comes to 60.19, which implies that only the aromatic chlorine

in DDT has undergone combustion to consume silver nitrate.

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The exchange equilibrium of heavier organic cations, like dimethyl ammonium, tetramethyl ammonium and tetraethyl ammonium, with cation-exchange resin prepared from waste acid sludge have been studied and the selectivity order was found to be of the following order : ammonium < dimethyl ammonium < tetramethyl ammonium < tetraethyl ammonium. Similar studies have been made with CNSL resin as well. Further studies have been made with different ammonium salts in order to determine the effect of anions on exchange of ammonium ions. It has been found that the change in equilibrium constant due to change of anions is quite negligible.

Studies on Cation-Exchange Resin from Waste Acid Sludge—Equilibrium with Large Organic Cations

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The exchange of organic cations from aqueous solution of their hydrochlorides with calcium zeolite was studied by Ungerer¹ but his results were quite complicated because of simultaneous exchange of hydrogen ion produced from hydrolysis of salt. In the present study hydrogen ion has been eliminated by taking neutral salts and all the organic cations have been used in their chloride form only, although it has been established here that change of anion in exchanging salt solution does not affect the equilibrium which remains constant.

The affinity of some large organic cations, like quaternary ammonium salts and quininium ion, for a phenol sulphonate resin has been studied by Kressman and Kitchner², who found that it increases with the size of ion, the effect being largely contributed by Van der Waal's forces. No change was noticed by them in saturation capacities even with the largest of quaternary ions.

Similar results were obtained with sulphonated polystyrenes of low crosslinkings, but with resins of high crosslinking, affinity considerably decreased with increase in ionic size³. Over a wide range of crosslinking the rate of exchange of quaternary ammonium ions on sulphonated polystyrenes decreases with increase in ionic size and degree of crosslinking. Various studies²⁻⁷ were made earlier for absorption of organic ions with polystyrene base cation-exchange resins. In their

studies⁴ on absorption of quaternary ammonium ions by sulphonated polystyrene resins of different crosslinking, Hale *et al*⁴ found that the absorbed amount decreased with increase in degree of crosslinking of resin and in general with the size of organic cation, and noted a marked dependence of absorption of the quaternary ammonium ions of pH.

Studies have been carried out in this laboratory in continuation of the earlier studies⁸ on cation-exchange resin from waste acid sludge where the equilibrium of univalent and bivalent ions have been dealt with hydrogen form of resin. The exchange of dimethyl ammonium tetramethyl ammonium and tetraethyl ammonium ions have been studied here with hydrogen form of the exchanger, the parent ammonium ion being used as a reference ion. Similar studies have been made with other polyfunctional resin, viz. CNSL resin, for comparison purposes. In order to find out the effect of anions on exchange of ammonium ions with exchanger, studies have been made by taking different ammonium salts, like ammonium sulphate and ammonium nitrate.

Experimental

After soaking completely with water, the samples of both the cation-exchange resins, viz. Sindex-C 26 and CNSL resin, were reduced to —20+22 mesh (BSS). The sieved samples were then conditioned as mentioned earlier⁸. Analytically pure or high grade

(C.P.) chemicals were used throughout the experiment. All the solution used here have been standardized by the normal procedure.

Method

The moisture content of the air-dried resin in hydrogen form was determined by drying a weighed sample of the resin to a constant weight at 105-110°C. About 1g. of each air-dried sample was accurately weighed and transferred to 200 ml. glass-stoppered air-tight bottles. Different volumes of accurately measured 0.1 N solution of organic salts were then added to the bottles and adjusted to 100 ml. by adding 0.1 N hydrochloric acid.

The time of attainment for equilibrium was given 48 hours, as it had been seen that even for heavier organic cation, viz. tetraethyl ammonium ion, the reaction was over within this time. These solutions were decanted and aliquot portion of solution drawn for determination of acidity which was generated due to exchange of cations with hydrogen form of resin. It was already seen that molecular sorption of electrolyte itself which might have been there will not affect the equilibrium constant. After determining the concentration of salts in solution phase at equilibrium, the concentration of organic ion in resin phase was determined by difference. The equilibrium constant

was determined for a particular cation by knowing the concentration of metallic ion in both resin and solution phase and by applying the equation used earlier⁸. The results are given in Table 1.

Experiments have also been carried out for exchange equilibrium of heavier organic ions with other polyfunctional cation-exchange resin, viz. Tulsion-14 made from CNSL. The results are summarized in Table 2.

Further, in order to determine the effect of change in anions, different ammonium salts, like ammonium sulphate and, ammonium nitrate, were taken in place of ammonium chloride and their exchange equilibria studied in the same manner (Table 3).

Results and Discussion

It can be seen from the results (Table 3) that the effect of anions other than chloride associated with ammonium ions on equilibrium constant was quite negligible so either of the two ammonium salts could be taken for studying the exchange equilibrium. But to maintain uniformity, all the quarternary and secondary ammonium salts were taken in chloride form only.

It was found that as the ions were made larger, the rate of exchange became less in spite of higher affinity because of difficulty of diffusing into resin.

TABLE 1—EQUILIBRIUM CONSTANTS OF HEAVIER ORGANIC AMMONIUM IONS WITH CATION-EXCHANGE RESIN, SINDEK-C26
[Resin Size: -20+22 mesh (BSS); Temperature: 40°±0.1°C]

Sl. No.	Exchange Equilibrium of Salt	Ionic Fraction in Resin Phase X_R	Ionic Fraction in Solution Phase X_S	Equilibrium Quotient, K_a	Log K_a	Equilibrium Constant, K
1.	$H^+ \text{---} NH_4^+$	0.6490	0.6762	0.8856	-0.0528	1.025
		0.5038	0.5380	0.8726	-0.0592	
		0.3678	0.3360	1.150	+0.0607	
		0.2072	0.1635	1.337	+0.1261	
2.	$H^+ \text{---} Me_2NH_3^+$	0.7065	0.6581	1.250	0.0969	2.291
		0.6070	0.4802	1.672	0.2232	
		0.4828	0.3065	2.112	0.3247	
		0.3412	0.1328	3.384	0.5294	
3.	$H^+ \text{---} Me_4N^+$	0.7467	0.7294	1.093	0.0389	2.691
		0.6434	0.5346	1.557	0.1923	
		0.5158	0.3498	1.980	0.2967	
		0.4200	0.1609	3.778	0.5772	
4.	$H^+ \text{---} Et_4N^+$	0.7949	0.6873	1.763	0.2463	8.030
		0.7196	0.4977	2.592	0.4136	
		0.6304	0.3099	4.015	0.6036	
		0.5072	0.1262	6.998	0.8450	

TABLE 2—EQUILIBRIUM CONSTANTS OF HEAVIER ORGANIC AMMONIUM IONS WITH CNSL CATION-EXCHANGE RESIN
[Resin Size: -20+22 mesh (BSS); Temperature: 40°±0.1°C]

Sl. No.	Exchange Equilibrium of Salt	Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution Phase, X_S	Equilibrium Quotient, K	Log K_a	Equilibrium Constant, K
1.	$H^+—NH_4^+$	0.6702	0.6642	1.027	0.0116	1.150
		0.5140	0.4953	1.077	0.0322	
		0.3825	0.3225	1.301	0.1142	
		0.2195	0.1555	1.527	0.1838	
2.	$H^+—Me_2NH_2^+$	0.6911	0.6651	1.126	0.0515	1.758
		0.5466	0.4824	1.293	0.1116	
		0.4565	0.3079	1.888	0.2760	
		0.3021	0.1375	2.715	0.4338	
3.	$H^+—Me_3N^+$	0.6885	0.6540	1.169	0.0678	2.113
		0.5973	0.4740	1.645	0.2162	
		0.4695	0.2961	2.105	0.3232	
		0.3129	0.1332	2.963	0.4717	
4.	$H^+—Et_4N^+$	0.7403	0.6556	1.497	0.1752	5.370
		0.6615	0.4698	2.206	0.3436	
		0.5735	0.2881	3.323	0.5215	
		0.4534	0.1103	6.689	0.8254	

TABLE 3—EFFECT OF DIFFERENT AMMONIUM SALTS ON EQUILIBRIUM CONSTANT FOR CATION-EXCHANGE RESIN, SINDEK-C26
[Resin Size: -20+22 mesh (BSS); Temperature: 40°±0.1°C]

Sl. No.	Exchange Equilibrium of Salt	Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution Phase, X_S	Equilibrium Quotient, K	Log K_a	Equilibrium Constant, K
1.	NH_4Cl	0.6490	0.5762	0.8856	-0.0528	1.025
		0.5038	0.5380	0.8726	-0.0592	
		0.3673	0.3360	1.150	+0.0607	
		0.2072	0.1635	1.337	+0.1261	
2.	NH_4NO_3	0.6782	0.7110	0.8567	-0.0672	1.060
		0.4333	0.5345	0.8826	-0.0542	
		0.3604	0.3463	1.0640	+0.0268	
		0.1632	0.1253	1.3610	+0.1340	
3.	$(NH_4)_2SO_4$	0.6131	0.6703	0.7795	-0.1082	1.047
		0.4896	0.5104	0.9200	-0.0362	
		0.3645	0.3322	1.153	+0.0618	
		0.2162	0.1600	1.448	+0.1609	

So the time for equilibrium was given here as 48 hours within which the equilibrium was completely attained with tetraethyl ammonium ions. No physical absorption of organic cations or salt occurred even when cation was large, presumably because of nearly complete dissociation of these salts. As it is evident from the Table 1, the order of selectivity of different quaternary and secondary ammonium ions studies here were found to be in the following order: ammonium < dimethyl ammonium < tetramethyl ammonium < tetraethyl ammonium. As the ions became heavier, their affinity for the ion-exchange resin increased. Similar results were obtained with CNSL resin also selected here for comparison. The affinity as measured by equilibrium constant increased with ionic size. It showed that ion was held by different set of forces from those binding simple inorganic ions, where affinity decreased with increasing size and suggested that Van der Waal's forces were contributing considerably to affinity while Coulumb forces predominant in determining affinity of inorganic cations were playing a minor role. In this respect, the behaviour of large ions towards resin is similar to that of a dye ion towards a textile fibre.

Further, the saturation capacities for heavier organic ions were also found to be the same in all the cases.

It clearly showed that the size of all the ions selected here were less than that of smallest molecular pore within the resin.

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A method for obtaining different forms of hydrated and anhydrous oxides of iron is reported. Starting from alkali-treated ferrous and ferric salts, α , β , γ and δ -FeOOH as well as ϵ -Fe₂O₃ have been obtained by employing different current densities and pH of the suspension.

An Improved Method for Rapid Preparation of Different Modifications of Oxy-Hydrate of Iron

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Iron forms a number of oxides and hydrated oxides, most of which find extensive commercial application. Haematite and β -FeOOH are used in paint industry, maghaemite, magnetite and ϵ -Fe₂O₃ find use as magnetic recording materials and in electronic industry. Goethite is utilized in chemical industry for removal of hydrogen sulphide while β -FeOOH is suitable for sulphur dioxide adsorption¹.

In general, the hydrated oxides are prepared by treating ferrous or ferric hydroxide with different oxidizing agents. The strength of the oxidizing agent, presence of foreign ions and the pH of the dispersing medium determine, to a large extent, the form of the hydrated oxide obtained, although the underlying mechanism is not very well understood. For example, aerial oxidation of the hydroxides at pH > 7 produces α -FeOOH, while at pH < 7 and in presence of chloride ions β -FeOOH is obtained². A rapid oxidation of Fe (II) hydroxycomplexes with hydrogen peroxide results in the formation of δ -FeOOH³.

Usually the preparation is a very slow process, requiring hours and often days for completion. While the actual process is very complicated involving too many parameters, the strength of the oxidizer appears to play a very important role. It is also evident that while the control of other bulk parameters like pH and temperature is comparatively easy, a close control of the oxidation process is much more difficult. It is known from a large number of instances that anodic oxidation in an electrolytic cell may be as effective as any chemical oxidizer. Moreover, with anodic oxidation, a much

better control can be achieved through manipulation of e.m.f. and current density. The same process applied to the preparation of the various oxides and hydrated oxides of iron is expected to exhibit a better control on the nature of the end-product and at the same time accelerate the reaction in many cases. With this view, attempts were made to precipitate out these compounds in an electrolytic cell. The results proved very encouraging.

Some Typical Examples

1. The preparation of goethite (α -FeOOH) by aerial oxidation of ferrous hydroxide requires several days. By electroodic oxidation process, the reaction time could be brought down to a few hours.

0.1 M aqueous solution of Fe(NH₄)₂ (SO₄)₂ was treated with ammonium hydroxide to bring the pH to 7. Platinum electrodes were connected to a constant current source and the electrode area was adjusted to obtain a current density of 6 mA/cm². The reaction was complete within 10 hr. The precipitate, after washing and drying at 50°C, was found to be goethite in pure form, as determined by x-ray diffraction and thermomagnetic analysis.

2. 0.005 M Fe(NH₄)₂ (SO₄)₂ solution, treated with liquor ammonia to obtain pH 7 was similarly subjected to electrolytic oxidation. A current density of 2mA/cm², applied for 36 hr. produced yellow precipitate of β -FeOOH.

3. A similar solution at pH 8 conducting a current density of 20 mA/cm², precipitated out lepidocrocite

(γ -FeOOH) within 1 hr. γ -Fe₂O₃ can be obtained by heating γ -FeOOH at 300°C for an hour.

4. 3M ferric chloride solution was treated with caustic soda to obtain a strongly alkaline suspension of ferric hydroxide at pH 10. Electrode oxidation at a current density of 60 mA/cm² formed the black ferromagnetic δ -FeOOH in 1 hr.

5. A current density of 100 mA/cm. passing through a .005M solution of Fe(NH₄)₂ (SO₄)₂, treated with caustic soda to bring the pH to 11 resulted in precipitation of ϵ -Fe₂O₃ in 10 min.

Besides the current density and pH, the electrode material also has a pronounced effect on the resultant phase. The mild steel electrode plates used in the electrolytic cells tend to produce Fe₃O₄, whereas with

platinum or stainless steel electrodes this phase was not observed.

This process has significant potentiality in the industrial manufacture of the various forms of oxides and there is scope for extensive investigations in this field.

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Five sources of nitrogenous and two sources of phosphatic fertilizers were tested during 1970-71 and 1971-72 on Sioux variety of tomato with a view to find out their relative efficacy. Ammonium sulphate nitrate gave the highest yield when averaged over the phosphatic sources, while calcium ammonium nitrate was found at par. Treatment with ammonium bicarbonate in combination with single superphosphate (SSP) gave significantly the lowest yield than those of others. Between the phosphatic sources a slight superiority of SSP over Suphala was observed but its use was advocated in a suitable combination with nitrogenous fertilizers without any appreciable decrease in yield of tomato.

Efficacy of Different Forms of Nitrogenous and Phosphatic Fertilizers on Tomato: (*Lycopersicon esculentum* Mill.)

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Tomato, one of the important vegetables, requires large quantities of available plant nutrients. It responds well to balanced application of fertilizers for proper growth and optimum production. Although some information on the optimum NPK requirements of this crop is available,¹⁻⁴ experimental evidence about the efficiency of the different sources of nitrogenous and phosphatic fertilizers currently available in the market is very scanty. As such, the present experiment was conducted to find out the relative efficacy of five sources of nitrogenous and two sources of phosphatic fertilizers on tomato.

Materials and Methods

Sioux variety of tomato was used with five sources of nitrogenous fertilizers, viz. ammonium bicarbonate (ABC), ammonium sulphate (AS), ammonium sulphate nitrate (ASN), urea (U) and calcium ammonium nitrate (CAN) and two types of phosphatic fertilizers, viz. single superphosphate (SSP) and 20:20:0 grade of Suphala. Uniform doses of N, P and K at the rate of 100 kg. N/ha, 25 kg. P/ha and 45 kg. K/ha were applied. 50 per cent of nitrogen and whole of phosphorus either from Suphala or SSP and whole of potassium from muriate of potash were applied as basal dose. The rest 50 per cent of nitrogen was applied 40 days after transplanting as top dressing with different sources of nitrogenous fertilizers.

The experimental design followed was randomized block with three replications. Thirty days old seedlings were transplanted at a spacing of 60 cm. both ways. The net plot size was 21.6 sq. m and 60 seedlings were planted in each plot. The trial was conducted for two consecutive seasons, viz. 1970-71 and 1971-72. Standard cultural practices were followed. The soil of the experimental plot was ash grey coloured, sandy loam and detailed soil analysis data are presented in Table 1.

TABLE 1—CHEMICAL CHARACTERISTICS OF SOIL

Available N, %	..	0.022
Organic Carbon, %	..	0.224
Available P, kg. /ha.	..	6.98
Available K, kg./ha.	..	130.50
pH	..	7.5
Electrical Conductivity, m. mhos/cm.		0.50

At the flowering stage, five plants were selected at random from each treatment; they were severed at the ground level, chopped, oven-dried, grinded and used for analysis of nitrogen, phosphorus and potassium contents. The total nitrogen was analysed by micro-Kjeldahl's method. Phosphorus and potassium were extracted from plant sample by digesting it with tri-acid mixture. From the extractant, phosphorus was

determined colorimetrically and potassium with flame photometer.

Results and Discussion

Fruit yield data of both the years were pooled, statistically analysed and are presented in Table 2.

From Table 2 it may be seen that of all the nitrogenous fertilizers, ASN treatment produced the highest yield (44.07 te/ha) when averaged over the phosphatic sources and it was found significantly superior to all other treatments excepting CAN, which was however, found to be at par.

TABLE 2—YIELD OF TOMATO TO DIFFERENT NITROGENOUS AND PHOSPHATIC FERTILIZERS, TE/HA

Nitrogenous Forms	Ammonium Bicarbonate	Ammonium Sulphate	Ammonium Sulphate Nitrate	Urea	Calcium Ammonium Nitrate	Mean
Single Superphosphate (SSP)	31.69	42.64	48.79	41.40	43.89	41.67
Suphala	40.15	37.19	39.41	42.09	41.26	40.01
Mean	35.90	39.92	44.07	41.76	42.55	40.84

C.D. for interactions : 2.50 te/ha.

C.D. for nitrogen mean : 1.77 te/ha.

C.D. for phosphatic mean : 1.19 te/ha.

ABC in combination with SSP gave the lowest yield. However, this effect was not found in Suphala and ABC combination.

ABC was found superior to AS and urea in paddy when applied in solution form to the root zone because of the increased intake of NH_4 ion as a result of considerable carbon dioxide fixation by roots⁵. In the present experiment also, although fertilizers were well mixed with the soil surrounding the root regions of the plants followed by irrigation, the performance of ABC was found significantly superior to AS when applied in combination with suphala and it was at par with ASN and Urea when applied in combination with suphala.

Geraldson and Kelbert⁶ observed the superior effect of sodium nitrate over ammonium sulphate in tomato. According to Westgate and Forbes⁷ nitrate of soda and ammonium nitrate were significantly better sources of nitrogen than AS in cabbage. From the present experiment, it is evident that nitrogenous fertilizers containing nitrate component proved to be better as compared to that containing ammoniacal form only. Hence, it is apparent that the superiority of ASN towards

greater production of tomato might be due to the presence of nitrate component in ASN and CAN. Twyford⁸ and Bid and Das⁹ found ASN a better nitrogenous source for banana. In tomato also ASN proved to be a better nitrogenous source. But from nutritional point of view, tomatoes have apparently no marked preference for either nitrate or ammoniacal nitrogen¹⁰. Hence, the authors presume that besides the anion and cation forms of nitrogenous fertilizers, some unknown reasons determine their efficacy.

The poor performance of ABC in combination with SSP required further study so as to point out clearly whether it is due to non-nitrate form of nitrogen or possible interaction with SSP.

Between the phosphatic sources, although no appreciable difference between SSP and Suphala was noticed in some treatment combinations, pooled data, however, indicated slight superiority of SSP to Suphala when averaged over the sources of nitrogen. ASN and SSP combinations, however, gave the highest yield (48.79 te/ha) of all other treatment combinations and it was consistent in both the years.

The authors had observed^{11,12} that nitrophosphate behaved as good as straight nitrogenous fertilizers in combination with SSP in water melon and lady's finger. In the present experiment in tomato, a slight superiority of SSP over Suphala was reflected towards yield, when averaged over nitrogenous fertilizers. But, these two phosphatic fertilizers responded differently in combination with different nitrogenous fertilizers.

A combination of Suphala and urea produced tomato to the extent of 42.09 te/ha, and this treatment gave an increased yield by 1.4 per cent over that of SSP and urea in combination. This indicates to choose the correct combination of nitrogenous and phosphatic sources in tomato culture without losing appreciable yield keeping in view that production of Suphala does not involve any import of sulphur through foreign exchange.

The year-effect was found significant showing that in one year, the yield was slightly more than that of the other but interaction between yield and treatments, being non-significant, indicated that the trend of response in both the years was of the same order.

NPK Content of Plant Samples

Plant samples from each treatment were collected at flowering stage. The contents of nitrogen, phosphorus and potassium were determined in both the years and the average figures are presented in Table 3.

TABLE 3--AVERAGE CONTENT OF N, P, AND K OF TOMATO-PLANT OF OVEN-DRIED MATERIAL AT FLOWERING STAGE, %

Nutrient	Forms of N Forms of P	Ammonium Bicarbonate	Ammonium Sulphate	Ammonium Sulphate Nitrate	Urea	Calcium Ammonium Nitrate	Mean	S. E. of mean
N	S.S.P.	3.17	3.29	3.44	3.21	3.43	3.31	± 0.19
	Suphala	3.23	3.04	3.34	3.27	3.33	3.24	
	Mean	3.20	3.17	3.39	3.24	3.38	3.28	
P	S.S.P.	0.54	0.54	0.66	0.60	0.60	0.59	± 0.12
	Suphala	0.51	0.53	0.56	0.55	0.62	0.55	
	Mean	0.53	0.54	0.61	0.58	0.61	0.57	
K	S.S.P.	0.57	0.59	0.73	0.53	0.75	0.63	± 0.13
	Suphala	0.50	0.62	0.67	0.68	0.76	0.65	
	Mean	0.54	0.61	0.65	0.61	0.76	0.64	

The uptake of nitrogen, phosphorus and potassium by plants at flowering stage expressed as percentage did not show any significant difference due to various treatment combinations in any of the years tried.

The nutrient status of plants at flowering stage greatly reflects on the production of fruits. In the present experiment the percentage difference of N, P and K content of plants under different treatments were non-significant but a trend was observed corresponding to yield. The highest nutrient content of nitrogen, phosphorus and potassium was found under ASN treated plants which produced the maximum yield and that of CAN was next to it.

Acknowledgement

The authors' thanks are due to Sri K. P. Dasgupta, Senior Statistician, for designing the experiment and to the staff of Horticultural Section for assisting in various ways for conducting the experiment.

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[Original mss. received on June 12, 1974]

Molybdenum is estimated as diaquo bis-2-amino-1-cyclopentene-1-dithiocarboxylate molybdenum (II). This compound has been analysed and a tentative structure is proposed.

Gravimetric Estimation of Molybdenum by 2-Amino-1-Cyclopentene-1-Dithiocarboxylate

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Introduction

Ammonium-2-amino-1-cyclopentene-1-dithiocarboxylate forms a number of bivalent and trivalent metal complexes^{1,2}. In the present work, molybdenum has been estimated as diaquobis-2-amino-1-cyclopentene-1-dithiocarboxylate molybdenum (II). It forms a very stable complex with the above ligand, and hence the latter has been used for the gravimetric estimation of molybdenum, when other metals are absent. This compound was analysed and its magnetic susceptibility and infrared spectra were studied.

Experimental

To a solution of ammonium molybdate having a known amount of the substance, an excess of aqueous ammonium-2-amino-1-cyclopentene-1-dithiocarboxylate solution was added. Acetic acid was then added to bring the pH in the range 5-6 during which the temperature was not allowed to rise above 20°C. The brown compound of molybdenum-2-amino-1-cyclopentene-1-dithiocarboxylate was filtered, washed several times with water and dried over fused calcium chloride in a vacuum desiccator. It was then analysed for molybdenum, nitrogen, and sulphur by the usual methods⁴. The infrared spectra of the compound was studied in solid potassium bromide in Perkin-Elmer Infrared Spectrophotometer-421 model.

Results and Discussion

The results (Table 1) show that molybdenum can be estimated from its soluble salts by using ammonium-

2-amino-1-cyclopentene-1-dithiocarboxylate. The analytical data and infrared spectra studies are summarized in Tables 2 and 3 respectively.

TABLE 1—ANALYSIS OF KNOWN COMPOUND

Amount of Ammonium Molybdate Taken, g.	Molybdenum in Ammonium Molybdate, %	Molybdenum Found After Complex Formation, %
0.2396	1.302	1.300
0.2105	1.143	1.139
0.2403	1.305	1.301

TABLE 2—ANALYSIS OF MOLYBDENUM COMPLEX

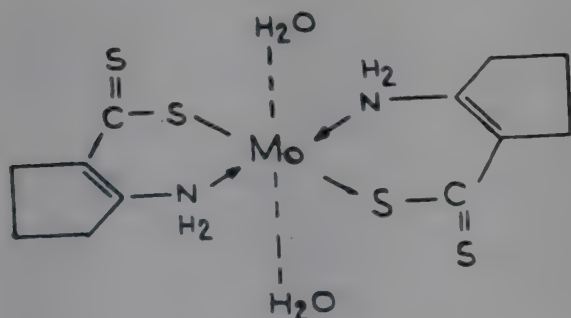
Compound Formula	Calculated Value, %			Experimental Value, %			μ eff
	Mo	N	S	Mo	N	S	
MoL ₂ ·2H ₂ O	21.39	6.247	28.61	21.35	6.201	28.50	dia.

TABLE 3

	(NH ₂) ν cm. ⁻¹	(NH ₂) ν cm. ⁻¹	C=S cm. ⁻¹	C-N/ C=S cm. ³ m.	C-S, c ⁻¹
Ligand	3480-S 3279-S 3100-S	1647-S	1538-m 1460-S 1449-S 1418-S	1370-S 1319-ms 1290-S	795-S
MoL ₂ ·2H ₂ O	3400-Br 3190-S	1610-S	450-S 1400-S	1375-S 1320-S 1280-S	830-S

The infrared spectra of the ligand¹ and its metal complex show asymmetric and symmetric stretching vibrations, deformation vibration of NH_2 group, $\text{C}-\text{C}$, $\text{C}-\text{N}$ and $\text{C}-\text{S}$, H_2O . The band which was observed in the region 3100 to 3480 cm^{-1} in the case of ligand¹, was lowered down to 3400 cm^{-1} in the case of molybdenum complex and became broad. This lowering of band indicates that the metal was co-ordinated to NH_2 group and H_2O of the ligand³. A strong band at 795 cm^{-1} of the ligand is attributed to $\text{C}-\text{S}$ stretching vibration, which shifted to a higher frequency in the case of the molybdenum complex indicating that the molybdenum is co-ordinated through $\text{C}-\text{S}$ group⁸.

From this infrared study, it appears that the molybdenum complex is formed through H_2O , NH_2 , $\text{C}-\text{S}$ group of the ligand and stoichiometric formula may be written as $\text{MoL}_2\cdot 2\text{H}_2\text{O}$ (where $\text{L}=\text{ligand}$). Hence, the structure may be written as



It was observed from the analysis (Table 1) that the amount of molybdenum taken for analysis was found to be same in molybdenum complex with an error of ± 0.002 per cent, so this indicates that molybdenum could be very well estimated as diaquobis molybdenum-2-amono-1-cyclopentene-1-dithiocarboxylate.

Conclusion

From the experimental data we came to conclusion that molybdenum can be estimated quantitatively from its soluble salt by using ammonium-2-amono-1-cyclopentene-1-dithio carboxylate. The diamagnetic property of molybdenum complex also indicates the octahedral structure of the complex and the characteristics of the compound is established. As the ligand forms the stable complex with molybdenum, if the experimental conditions are maintained properly, then this ligand can very well be used in the gravimetric estimation of molybdenum.

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The severity of the pink bitter core rot disease of *Averrhoa Carambola* fruits from Faizabad caused by *Trichothecium roseum* has been studied for the first time.

Market Pathology of Faizabad Part 1—Virulence of Pink Bitter Core Rot of Kamrakh *Averrhoa Carambola* L

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Introduction

Tandon and Kakkar¹ for the first time reported incidental occurrence of *T. roseum* on the fruit of *Averrhoa Carambola* L. (Kamrakh) from Allahabad (U.P.). In the present communication the authors have reported the severity of the disease after making an extensive survey of fruit market of Faizabad.

Results & Discussion

Extensive survey of Faizabad (U.P.) vegetable and fruit-market, during August-November 1972, showed the virulence of this disease. Almost all the fruits were infected and became unfit for consumption. The first appearance of disease was recorded in August 1972 when the magnitude of infection was low. In September the infection was severe and it was recorded on more than 80 per cent fruits in all lots. In the succeeding months, however, the severity of infection exhibited a decreasing tendency and during November in all the lots it was below 30 per cent (Table 1). In most of the cases, the lesions consumed one-third to three-fourth part of the fruit rendering them useless. The disease starts from any point of injury on the surface of the fruits. The first symptom is a brown lesion, which radiates from the point of infection with invasion of tissues and instead of gradually spreading over the epidermis goes deep into the fruit and decomposes nearly the entire flesh, simultaneously producing a soft watery light brown fluid (Fig. 1). Thereafter, the massive production of the pink coloured conidia of *T. roseum* becomes visible on the surface of the fruits. In the advanced stage, a discoid sporulation of light pink conidia appears. The pink coloration and powdering extreme with age.

TABLE 1—INCIDENCE OF PINK BITTER CORE ROT OF *A. Carambola* AT DIFFERENT TIME INTERVALS

Months (1972)	<i>Averrhoa Carambola</i> Lots				
	1	2	3	4	5
August	36	49	39	31	26
September	97	85	80	92	80
October	55	51	45	49	23
November	29	19	23	16	18

Note: Figures indicates the percentage of infection (Average of 300 fruits sampled at random in different months.)

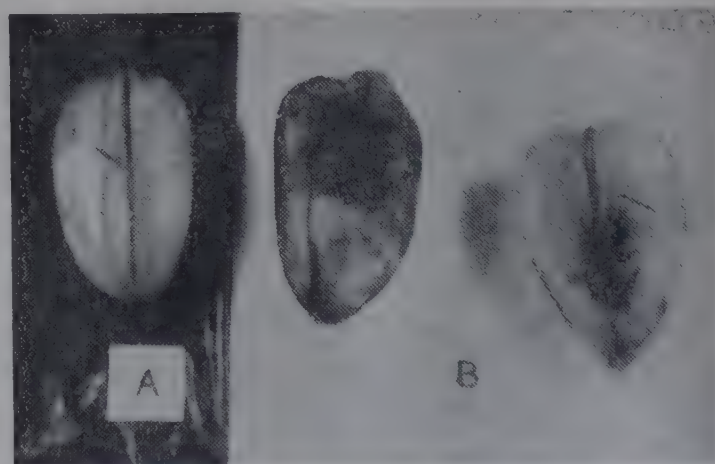


Fig 1—Fruits of *Averrhoa Carambola* Infected with *T. roseum*
A=Healthy, B (right) 4 Days' Old Infection and
B (left) 2 Days' Old Infection.

Sugars and organic acids, viz. citric and tartaric acids, are the main constituents of the fruits that are

readily utilized by *Trichothecium roseum*. The present survey shows that the extent of damage to fruit depends upon the duration of the storage and environmental conditions, particularly the temperature prevailing during marketing and this is the probable reason for high disease index during the September 1972 and comparatively lesser in succeeding months (Table 1). In fruits infected with *T. roseum*, secondary organisms became quickly established producing light brown fluid (Fig. 1). This secondary organism is supposed to be bacterium that appeared on the tissues killed by the advanced of the fungus towards the interior of the fruits emitting foul odour³.

Acknowledgement

The authors express their gratitude to Dr. R. S. Tewary, Principal, K. S. S. Post-Graduate College, Faizabad, (U.P.) for library and laboratory facilities.

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Sea as a Source of Sodium and Water as a Source of Fuel

Sodium exists as an ion in abundance in sea-water. As sodium ion, it is extremely useful to man to carry out his physiological functions. With the discovery of sodium metal, and its large-scale manufacture with the help of electricity, the price of sodium has come down to reasonable levels. It is a metal that reacts violently with water to produce hydrogen, which burns to form water, and in this process heat is produced. Thus, it becomes of interest to investigate the possibility of producing by electric current large quantities of sodium and use the sodium metal to produce hydrogen for heating purposes. In other words, one can visualize the possibilities of producing fuel from water through the medium of sodium metal. It may perhaps appear strange that one needs electric power to produce sodium and at the same time one uses sodium for producing fuel, which is generally used in producing electricity.

The strangeness of the situation may disappear when one considers the following technically weighed reasoning (i) the facilities of transferring energy in modern times from one location to another by way of electricity; (ii) the facilities of producing cheap electricity at central places most suitable for that purpose; (iii) the facilities to use electricity in large quantities to produce sodium from common cheap resources, like sea water at central places; (iv) difficulties and dangers of using sodium in large quantities at one place; (v) the advantages in the use of hydrogen at localized places as a fuel; and (vi) the possibilities of producing hydrogen from water by the use of sodium on a small scale.

In other words, the above idea is based on the use of cheap electricity at central places and the distribution of electricity by the way of sodium to centres where fuel is required. In this type of thinking, one can link up the advantages of the above proposal with the enormous disadvantages and cost one has to incur in the distribution of electricity for heating purposes.

In order to make progress in the development of this idea as mentioned above, we need methods: (1) to control the reactivity of sodium and water and (2) to

control the rate of combustion of hydrogen so that safe burners of hydrogen are available.

In terms of modern technology, these two are not problems requiring any great advance on the theoretical side. However, considerable experimental development work is necessary to bring the ideas into a practical shape. In this connection, one can take advantage of the modern methods of producing surface-active sodium and also take advantage of the enormous amount of fundamental work that have so far been carried out on the hydrogen oxygen reaction mainly to understand the combustion and explosion phenomenon. The practical work of this subject can be visualized to develop along the following lines:

1. Preparing thin layers of sodium metal uniformly distributed over an inert material, like aluminium oxide, and using fluidized beds of sodium coated aluminium oxide particles for preparing hydrogen.
2. Passing moist air through fluidized beds of sodium coated aluminium oxide to produce hydrogen-air mixtures at satisfactory rates without great rise of temperature of the fluidized beds.
3. Burning the hydrogen-air mixture in a burner in a safe manner. The scale of operation should be such that it can first be used in domestic applications in which case one can think of replacing the existing butane gases from petroleum refineries for domestic heating.

One of the difficulties that one can visualize is the utilization of sodium hydroxide that will form as a result of reaction of sodium and water. It is no longer a problem if one recognizes the need of sodium hydroxide for soap-making on a 'local' scale. Indeed, sodium reacts with equal ease in hydrochloric acid as in water. Hence, if dilute hydrochloric acid is chosen in the place of water the resultant sodium chloride-sodium hydroxide mixture can find a place in meeting the needs of sodium chloride and soda for domestic purposes on a local scale. It may be of interest to men-

tion that hydrochloric acid is a modern by-product of electrolytic sodium hydroxide industry.

For development work, one can consider also the addition of methane to hydrogen and the use of carbon dioxide to control the hydrogen-air reaction by carrying out investigations on the possibility of using enzyme reactions for methane as well as carbon dioxide preparation, along with the sodium-water reaction.

It is concluded that a new cycle for sodium element can be thought of, by taking it from sea with the help of electricity and using the metal sodium in millions of homes to generate hydrogen from water for fuel purposes and utilizing the sodium hydroxide-sodium chloride locally. The products of combustion of hydrogen is water and hence there is no problem of atmospheric pollution, when hydrogen is used as a fuel.

Sodium is well recognized as an important element essential for physiological functions and hence the above scheme can not be criticized on any account.

It is concluded that the extra research and development effort that has to be carried out to make this scheme a practical reality is really very small when compared to the benefits that are in store and when this idea is taken up in an active modern way.

The author thanks Dr. H. V. K. Udupa, Director, Central Electrochemical Research Institute, for his encouragement.

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The fertilizer programme considers fuel oil as the predominant feedstock for the future fertilizer projects. The oil crisis in late 1973 has raised doubts regarding the availability of petroleum products including fuel oil from indigeneous as well as imported sources. The prices of petroleum products are expected to prevail at much higher levels than now even if they are available. In the event of non-availability of fuel oil, or its availability at economically unattractive prices, one has to consider the possibilities of adapting these plants to other feedstocks that would be available indigenously. In the present context, a study on the implications of an eventual change-over to coal of a plant meant for operation on fuel oil is particularly relevant. In view of the lead time required for development of new coal mines, it will be necessary for the plant to operate on fuel oil initially, with the possibility of an eventual change-over to coal. The type of installations and process sequences which are typical of FCI plants for conversion of fuel oil to ammonia (partial oxidation under pressure, and coal to ammonia (coal dust gasification at atmospheric pressure) forms the basis of this study. The other possibility, like high pressure gasification of coal, has not been considered. The study confines its analysis to the technical and financial implications of change-over to coal for a plant meant for operation with fuel oil.

A Case Study of a Design of a Fuel Oil-Based Plant Keeping in View the Possibility of Eventual Change-over to Coal as a Feedstock*

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Introduction

The case study discussed here specifically relates to the adaptation of a fuel oil-based plant to coal on the basis that (i) fuel oil may not be available or its price may be uneconomical in future, (ii) it is advantageous to continue operation on fuel oil as long as it is available at economically attractive prices, (iii) the development of a coal mine for making available the requisite quantities of coal, when required, would take longer than the construction period of a fuel oil-based plant and, therefore, it may be necessary to operate the plant on fuel oil at least for the first few years of operation, (iv) the additions envisaged to adapt the plant to coal, when required, should be minimum, (v) the value of redundant equipment after change-over should be minimum, and (vi) the reliability, efficiency and flexibility of operation is not foregone when the plant is called into operation using either of the feedstocks.

*This paper was presented at the FAI Symposium on Coal as Feedstock for Fertilizer Production held at New Delhi during April 29-30, 1974. It is reprinted here with kind permission of the authors and of the Fertilizer Association of India, New Delhi.—Editor

Fuel Oil-Based Ammonia Plant

Fig. 1 gives the typical process sequence for a 900 tpd ammonia plant as adopted for a fuel oil plant (Haldia and Nangal). The plant consists of the following sections : (i) gasification of fuel oil and carbon recovery, (ii) desulphurization by cold methanol wash, (iii) CO-conversion, (iv) CO₂ removal by cold methanol wash, (v) liquid nitrogen wash, (vi) synthesis gas compression, and (vii) ammonia synthesis and storage.

Gasification and Carbon Recovery : For the production of raw synthesis gas by reacting the feedstock with controlled amounts of oxygen and steam in high pressure reactors, the fuel oil-based plants use an optimum pressure of about 55 atm. The cooling and cleaning of the hot gases provide for incidental recovery of high pressure steam at 105 ata for subsequent use for drives and process. The finely suspended soot is recovered by water scrubbing, collected from water slurry by pelletization with fuel oil and recycled to reactor by slurring with feedstock.

Gas Purification : The desulphurization of the raw gas from the gasification section is effected by methanol

wash along with sulphur recovery, subsequent to which carbon monoxide in the gas is converted to carbon dioxide and hydrogen in a high temperature CO-conversion unit. The carbon dioxide removal and recovery is effected in a cold methanol wash unit, whereafter the gas proceeds to a liquid nitrogen wash unit. All the purification steps outlined herein are effected at about 50 atm pressure.

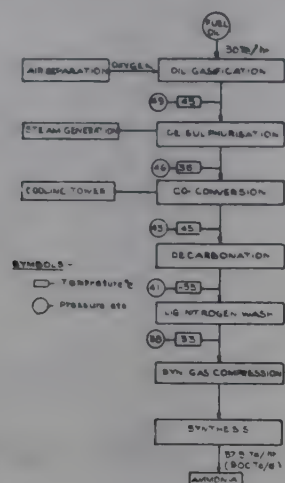


Fig. 1—Flow Diagram of a Fuel Oil-Based Ammonia Plant

Synthesis Gas Compression and Synthesis : The purified synthesis gas is compressed to synthesis pressure in a steam-driven centrifugal compressor for ammonia synthesis in a conventional unit.

Auxiliary Facilities : For a 900 tpd ammonia plant, the air separation plant with a capacity of 25,000 Nm³ per hr of oxygen provides the pure oxygen for gasification, pure nitrogen for liquid nitrogen wash, make-up for synthesis gas and for stripping weak Rectisol solution. The requirements of raw material and utilities for a plant of 900 tpd ammonia and 1500 tpd urea are summarized in Table 1.

Coal Based Ammonia Plant

Fig. 2 gives the typical process sequence for a 900 tpd ammonia plant based on coal (Talcher/Ramagundam). The plant consists of the following sections : (i) coal handling and preparation, (ii) coal gasification and cleaning of raw gas, (iii) raw gas compression, (iv) gas purification, (v) desulphurization, (vi) CO-conversion, (vii) CO₂ removal and (viii) liquid nitrogen wash and (ix) synthesis gas compression and ammonia synthesis.

Coal Handling and Preparation : An extensive storage and reclamation facility has to be provided for coal. In addition, the coal dust gasification process requires an elaborate pulverization, drying and conveying arrangement.

TABLE 1—RAW MATERIAL AND UTILITIES FOR FUEL OIL-BASED AMMONIA PLANT AND AFTER CHANGE-OVER TO COAL

Item	Unit	Fuel Oil Based (base case)	After Change-over to Coal	
			Alternative I	Alternative II
RAW MATERIAL				
1. Fuel Oil	te/hr	30.0	—	—
2. Coal :				
(a) For Gasification	te/hr	—	65.5	65.5
(b) For Steam Generation	te/hr	40.8	56.0	56.0
3. Oxygen	Nm ³ /hr	23,000	32,800	32,800
UTILITY				
1. Power	Kw.	25,000	40,000	40,000
2. Boiler Feed Water	M ³ /hr	105	165	165
3. Cooling Water Circulation	M ³ /hr	28,200	37,000	38,200
4. Raw Water	M ³ /hr	1,800	2,700	2,800
	MGD	9.5	14.3	14.8
5. Steam Generation (105 ATA) From Service Boiler	te/hr	183	260	261

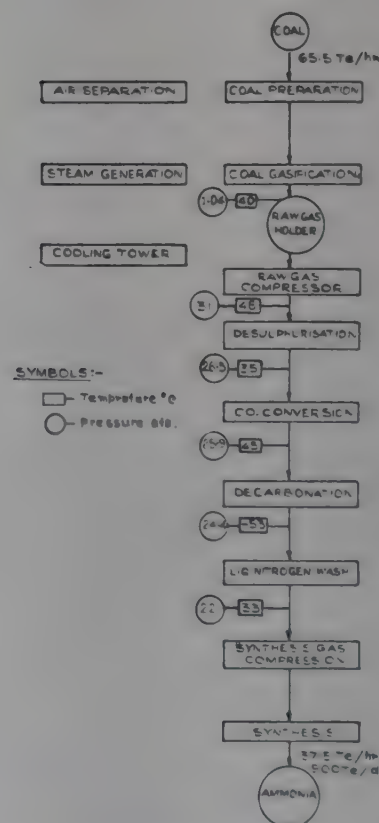


Fig. 2—Flow Diagram of Coal-Based Ammonia Plant

Coal Gasification and Gas Cleaning : The cooling and cleaning of gas from the atmospheric dust gasifier is effected in an arrangement consisting of waste heat boilers (steam at 105 atm), Thyssen washers and electrostatic precipitators to ensure complete removal of dust from the gas. The coal gasification as well as cleaning

steps are effected at atmospheric pressure. The raw gas is conveyed to a gas holder by means of a blower.

Raw Gas Compression and Purification : The purification steps involving desulphurization, CO-conversion, CO₂ removal and liquid nitrogen wash are identical in arrangement to a typical flow scheme adopted for the fuel oil plant, the only essential difference being the pressures of operation. The optimum pressure for purification steps for a coal-based plant is found to be about 30 atm, while the corresponding pressure for the fuel oil-based plant is around 50 atm. For this purpose, the raw gas at atmospheric pressure has to be compressed in a steam-driven centrifugal compressor to the process pressure.

Synthesis Gas Compression and Ammonia Synthesis : These steps are more or less similar to the fuel oil-based plant, except that the suction pressure for the synthesis gas compressor is about 30 atm. for a coal-based plant as compared to about 50 atm. for a fuel oil-based plant.

Auxiliaries : In addition, the quantities of oxygen, power, steam, water, etc. required for a coal-based project are higher than that for a fuel oil-based plant.

Change-over to Coal

The gas characteristics vary considerably depending on feedstock. Coal-based gas is leaner in composition with respect to potential hydrogen (measured as CO + H₂) and hence the volume to be handled for same ammonia capacity is higher by about 10 per cent over the oil-based operation. But the sulphur content is comparatively lower in coal-based gas.

The carbon monoxide-to-hydrogen ratio is higher in coal-based gas being roughly 1.8 as against 1.0 for fuel oil-based operation. This would require a bigger size carbon monoxide conversion unit with more catalyst and steam requirement and higher sized equipment and auxiliaries. As a consequence, the converted gas to be subsequently handled in decarbonation section is also 1.17 times the volume of corresponding oil based gas. It is richer in carbon dioxide, its content being 42 per cent in a coal-based case as against 33.5 per cent in an oil-based one. The decarbonation equipment also, therefore, require bigger sizing.

After decarbonation, both coal-based as well as fuel oil-based gas streams get to identical volumes and compositions and hence subsequent sections could be identical.

The oxygen requirement in case of coal-based operation is approximately 43 per cent higher than for corresponding fuel oil case. Hence, the air separation plant sizes differ substantially.

The service steam and the distribution for drives and process purposes also differ in either case.

From the above, it would be clear that for a change-over to coal, additions of coal preparation, coal gasification, and gas cleaning units to supersede the oil gasification unit are inevitable. To bring up the raw gas to processing pressure of the fuel oil-based train, provision of a suitable raw gas compressor is also necessary. Despite corrections in pressure, equipment upto the nitrogen wash group, however, would prove under-sized to handle the gas streams from a coal-based operation. To remedy this, two possibilities are open, viz. (i) to add to the individual sections, supplementary equipment to handle the extra gas volumes and altered compositions, and (ii) to do a pre-processing of the coal-based gas to get its composition and volume to correspond to those of the fuel oil-based gas and feed it at the appropriate point in the fuel oil-based train leaving operations in the latter unaffected.

In both the alternatives, the units for coal handling, for coal preparation, coal gasification and gas cleaning and the raw gas compressors would have to be installed. Besides, additional air separation units for the extra oxygen and nitrogen requirements, steam generation units for the extra steam requirements for process and drives, and additional facilities for water, power, etc. would be needed. Requirements of raw materials and utilities for the two alternative cases are presented in Table 1. The technical and financial implications of these alternatives are examined in greater detail.

Alternative 1—Additions in Individual Sections

Fig 3 describes the flow sequence to be adopted when the plant based on fuel oil switches over to coal. The additions for coal handling, preparation, gasification, etc. are shown. The pressure of raw gas is increased to about 50 atm. by the raw gas compressor and additions by way of individual equipment are foreseen in the different sections of the purification train.

Table 2 gives the relative dimensions of major equipment for the fuel oil case compared to the ones of additional equipment (major equipment) in different sections, if operations, based on coal, are to achieve the same rated capacity of ammonia and end-products.

Since the sizes of additional equipment to correct the capacity appear to be small when compared with the

original equipment, one could suggest that it may be worthwhile to size the plant in such a way even at the first instance for coal-based operations. When the plant uses fuel oil, these equipment would be oversized, but adequate for coal-based operation. The dimensions of major equipment in the different sections in such a case are also given in Table 2.

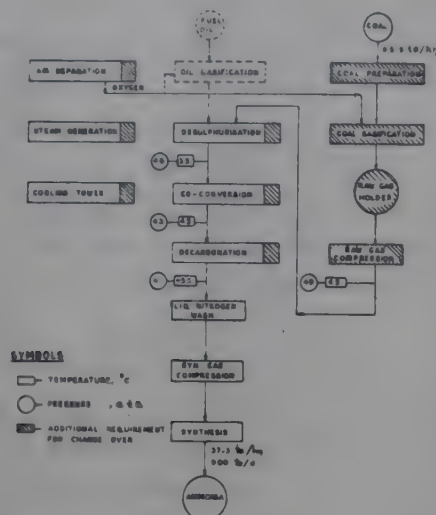


Fig. 3—Change-over to Coal as Feedstock—Alternative I
[Addition in individual purification section]

It may be seen from the above dimensions that the different equipment if provided as larger units at the first instance would be operating below their installed capacities when operated on fuel oil. In many cases, they would operate the optimum conditions of operation. This would lead to infructuous expenditure in the form of investment if the changeover to coal is not called for at a later date.

Alternative II—Pre-Processing of Coal-Based Gas to Correct Gas Composition and Volume

Fig. 4 shows the process flow sequence envisaged in the case of Alternative II. The entire gas from coal gasification unit after cleaning, is compressed to about 30 atm. in the raw gas compressor. About 25 per cent the gas is subjected to carbon monoxide conversion by which carbon monoxide in this particular stream is brought down to about 3.5 per cent from about 54 per cent but on mixing with the rest of the gas by-passing this carbon monoxide conversion unit, the average carbon monoxide content of the mixed gas is about 37 per cent. The entire quantity of this mixed gas is then subjected to carbon dioxide removal in a Benfield carbon dioxide removal unit by which, the gas at the exit of Benfield section is almost identical in composition and quantity to the raw gas from the fuel oil gasification. The pressure, which is only about 30 atm., is increased in a booster compressor, to about 50-55 atm.

TABLE 2—RELATIVE SIZES OF EQUIPMENT AFFECTED BY CHANGE-OVER TO COAL (ALTERNATIVE-I)

Sl. No.	Equipment	Fuel Oil-Based (base case)	Change-over to Coal		
			Additional equipment needed for change-over	If provision is made initially for change-over	Capacity limitation of base case equipment if used after change-over
					(per cent)
A. DESULPHURIZATION SECTION					
1.	Absorber	φ 100	53	112	17
		H 100	100	100	
2.	Heat Exchangers	A 100	11	111	11-12
B. CO-CONVERSION SECTION					
1.	Saturator	φ 100	52	113	23
		H 100	100	100	
2.	Shift Converter I	φ 100	53	108	23
		H 100	99	102	
3.	Shift Converter II	φ 100	51	109	23
		H 100	102	100	
4.	Cooler	φ 100	51	109	23
		H 100	100	100	
5.	Heat Exchangers	A 100	26	115	18-35
C. DECARBONATION SECTION					
1.	CO ₂ Absorber	φ 100	46	111	top 19
		H 100	100	100	bottom 47
2.	CO ₂ Flash Tower	φ 100	113	113	new for
		H 100	174	174	change-over
3.	Heat Exchangers :				
	(a) Shell & Tube Type	A 100	15	115	5-28
	(b) Wound Tube and Plate Type	Q 100	29	127	19-38

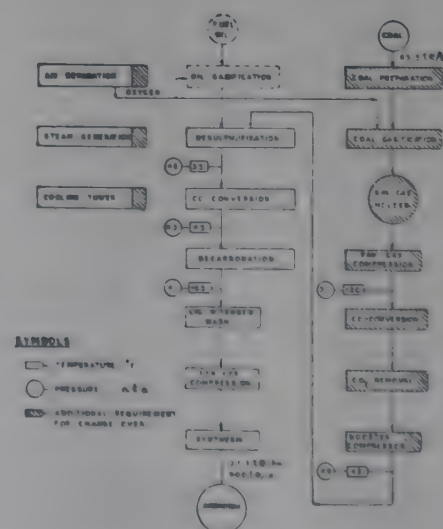


Fig. 4—Change-Over to Coal as Feedstock—Alternative II
[Additional purification stream to match the quality of raw gas.]

The corrected gas follows the steps of desulphurization, carbon monoxide conversion and carbon dioxide removal in the sections originally designed for fuel oil. In view of the corrective steps adopted to match the coal-based gas with the fuel oil-based gas in all respects of composition, volume and pressure, no additions/modifications are required in the purification steps to achieve the rated capacity.

One essential feature of both the alternatives is that the plant to be put up at the first instance when based on fuel oil does not involve changes in design from a standard fuel oil plant. If the operations are to continue on fuel oil (subject to its availability and at economical prices), the plant does not carry an infructuous/avoidable investment and does not incur higher operating costs in the absence of the said change-over.

The choice of the more suitable alternative between these available alternatives would depend on efficiency, reliability and flexibility in addition to economics.

Investment and Operating Costs

The details of investment requirements and operating costs for the standard fuel oil plant and the two alternatives are presented in Table 3. The fuel oil case has considered fuel oil at Rs. 250 and at Rs. 750 per tonne. From the above investment figures and operating costs, it is seen that the alternative involving additions in individual sections is slightly higher than the other alternative where the gas composition, volume and pressure are corrected. The difference is not significant enough to effect a choice between these two alternatives on financial considerations alone.

Alternative I would need modifications in almost all the existing sections of purification, calling for a number of interruptions involving a greater loss of production. In addition, in almost all the sections, each equipment has to be supplemented with a much smaller equipment of that type, which could pose problems in adjustment of gas flows in actual operation. From the point of view of engineering, Alternative II would be more advantageous since it involves only new sections. These come entirely outside the original plant. Interconnection would be necessary at only one point. From overall considerations, Alternative II is more favourable than Alternative I.

Timing of Change-over

As has already been stated, the change-over to coal may become inevitable in the event of non-availability of fuel oil. In such an event, the plant need not have to remain idle if the additional investment is made for

TABLE 3—INVESTMENT AND OPERATING COSTS

Item	Fuel Oil-based	After Change-over	
		Alter-native-I	Alter-native-II
A. INVESTMENT (Rs. millions)			
1. Fuel oil-based plant	1,277	1,277	1,277
2. Additional for change-over			
I. Coal gasification & purification	—	397	386
II. Other Facilities	—	103	102
Total investment	1,277	1,777	1,765
B. OPERATING COST (Rs./te Urea)			
1. Fuel oil price (Rs./te)	250	750	
2. Sales Realisation	1,050	1,050	1,050
3. Operating cost	844	1,100	1,037
4. Operating profit	206	(50)	13
			15

change-over to coal. But, there could be a situation when availability itself is not a problem, but that fuel oil would cost much higher than what is prevailing today. For instance, fuel oil which has been considered around Rs. 250 per tonne at present (exclusive of excise duty) may be available only at about Rs. 750 (the cost of the imported fuel oil as reported today). In such a case, one should be able to decide at what price of fuel oil would it be better to switch over to coal. Such an exercise has been carried out, taking the investment costs and operating costs for the preferred alternative, i.e. Alternative II. Such an exercise has been carried out for selling prices of urea, i.e. at a price of Rs. 1,050 (maximum retail price today), and Rs. 1,200 per tonne. This exercise has been done on the assumption that there may not be any increase in fertilizer prices commensurate with increase in feedstock costs. Fig 5 shows that at a selling price of Rs. 1,050 per tonne of urea, coal at Rs. 80 per tonne would break even with fuel oil at Rs. 555 per tonne. At selling price of Rs. 1,200 per tonne of urea, coal at Rs. 80 per tonne breaks even with Rs. 610 per tonne of fuel oil.

The internal rate of return for a fuel oil plant at today's price levels of feedstocks and fertilizers (Rs. 250 per tonnes of fuel oil and Rs. 1,050 per tonne of urea) is about 7.7 per cent. If this rate of return is to be maintained for the project, for all future prices of fuel oil,

there has to be an increase in the price of urea by about Rs. 250 per tonne (exclusive of excise duty) for every increase of about Rs. 500 per tonne for fuel oil. Fig. 6 indicates that it would be better to resort to change-over to coal (@ Rs. 80 per tonne) if fuel oil is to cost anything more than Rs. 795 per tonne. The price of Rs. 80 per tonne is considered high enough to allow for escalation in costs of coal in the coming years.

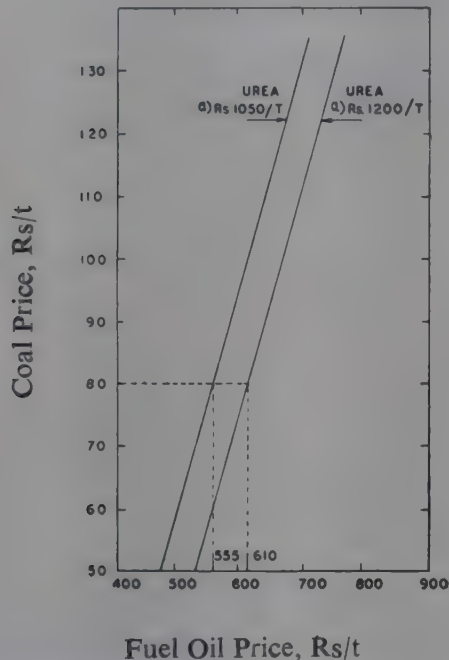


Fig. 5—Break-even Prices of Coal and Fuel Oil for Same Rate of Return
[At constant sale price of urea]

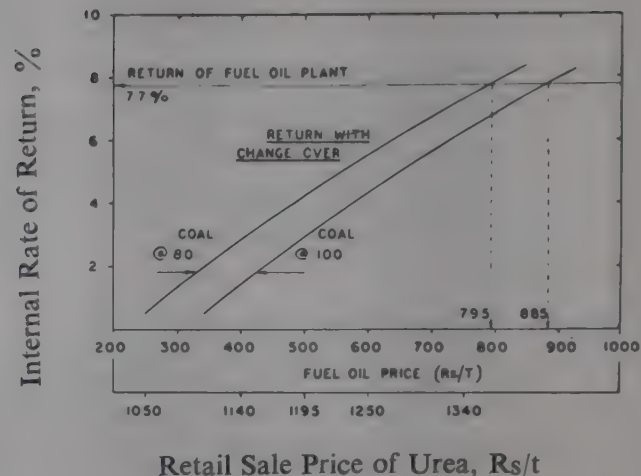


Fig. 6—Break-even Prices of Fuel Oil and Coal with Increasing Sale Prices of Urea commensurate with Increase in Fuel Oil Prices

Conclusion

From the above, it is seen that the design of fuel oil-based plant as is being considered for the present plants in India could be conveniently adapted to process coal without any technical problems. The alternative providing for pre-processing of coal-based gas to current composition, volume and pressure is considered to be more reliable, flexible and convenient. The additional facilities for change-over to coal would need at least a period of 30 months for design, engineering, construction and hooking up with the existing facilities. The need for and the timing of change-over would depend on whether fuel oil would be available and, if available, at what price.

The Central Fuel Research Institute (CFRI), since its inception, had been advocating conversion of the abundant resources of non-caking coals to synthesis gas/heating gas, adopting complete gasification techniques, to meet the ever expanding demand of fertilizers and development of coal-based gas industries for catering to the growing demand in the different regions of the country. Considerable pilot plant development work has been carried out in the field of complete gasification of coal for various industrial/domestic uses. This paper discusses the typical test results and salient features of pilot plant experiments conducted at this institute for studying the steam-oxygen gasification characteristics of Indian coals in suspended-bed gasifiers operating at atmospheric pressure and in fixed-bed gasifier operating at elevated pressures for production of synthesis gas and town gas. It also discusses broadly the influences of coal characteristics and operating conditions on the performances of different gasification processes and the fields of application of these processes for the development of coal-based fertilizer industry. Further research and development work needed for generation of synthesis gas economically is also indicated. It is strongly advocated that coal as a raw material should receive its due recognition, though belated, in the future development plans, especially for fertilizer industry.

Developmental Work on Complete Gasification of Indian Coals at CFRI*

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Disregarding the availability of large resources of coal, the planning for fertilizer production had shown a clear and distinct favour towards petroleum products as feedstock for fertilizer production in this country (Table 1). It was envisaged that by the end of 1978-79, when the fertilizer production would reach a level of 6 million tonnes of nitrogen, only about 15 per cent of the total requirement would be met from coal. But the recent oil crisis has put a wedge necessitating recasting of the previous planning. Sincere efforts should, therefore, be made for not only installing coal-based fertilizer plants in future, but also to reorient the existing plants to accept coal in place of petroleum as feedback.

In the absence of any large resources of oil or natural gas in the country, the CFRI had been advocating for adoption of complete coal gasification techniques for synthesis gas generation for fertilizer production. Basic as well as pilot plant studies on gasification characteristics of Indian coals were therefore initiated and tests conducted at this Institute in different units operating at atmospheric and at elevated pressures. The

scope of discussion in this paper has been limited to the salient features of gasification studies and the factors governing the development of large-scale coal-based fertilizer units in the country.

Complete Gasification of Coal

Since the Second World War, incentives towards total gasification of coal for production of synthesis gas and heating gas have increased and a number of processes for complete gasification of coal with steam and/or oxygen/air have been developed. These processes may be placed into the following categories: (i) processes where fuel is entrained in gas, e.g. down-draft gasification and Koppers-Totzek processes—suitable for caking or non-caking coal (size 80-90 per cent through 200 BS sieve); (ii) processes where the fuel is under fluidized conditions, e.g. Winkler process—suitable for non-caking reactive coals (size 10 mm-0); (iii) processes where the fuel is retained on a fixed bed, e.g. Lurgi process (pressure generator)—suitable for non-caking to weakly caking sized coals (size 3-25 mm.).

The only commercial complete gasification plant now under operation in India for fertilizer production is the Winkler generators at Neyveli (Tamil Nadu). Performance of these generators is not, however, satisfactory

*This paper was read at the FAI Symposium on Coal as Feedstock for Fertilizer Production held at New Delhi during April 29-30, 1974. It is reproduced here with kind permission of the authors and of the Fertilizer Association of India, New Delhi.

TABLE 1—NITROGEN CAPACITY BASED ON DIFFERENT FEEDSTOCKS

Feedstock	1955-56		1960-61		1965-66		1970-71		1973-74		1978-79	
	Quantity, 1000 tonnes	%	Quantity, '000 tes	%	Quantity, '000 tes	%	Quantity, '000 tes	%	Quantity, '000 tes	%	Quantity, '000 tes	%
1. Naphtha	—	—	—	—	112	19.1	803	59.7	1668	70.6	2321	38.7
2. Fuel oil/heavy stock	—	—	—	—	—	—	—	—	—	—	1677	27.9
3. Natural/associated gas	—	—	—	—	—	—	131	9.8	283	12.0	568	9.5
4. Coal	10*	10.4	10*	4.0	—	—	—	—	—	—	916	15.3
5. Coke	70	73.0	80	32.3	80	13.7	80	5.9	80	3.4	—	—
6. Lignite	—	—	—	—	70	12.0	70	5.2	70	3.0	70	1.2
7. Coke oven/refinery gas	—	—	47	18.9	212	36.2	152	11.4	152	6.4	115	1.9
8. Electrolytic hydrogen	1	1.0	91	36.7	91	15.6	88	6.6	88	3.7	88	1.5
9. Imported ammonia	—	—	—	—	—	—	—	—	—	—	225	3.7
10. By-product from coke oven gas	15	15.6	20	8.1	20	3.4	20	1.4	20	0.9	20	0.3
Total	96	100.0	248	100.0	585	100.0	1344	100.0	2361	100.0	6000	100.0

* Wood gasification.

TABLE 2—KOPPERS-TOTZEK GASIFICATION PLANTS*

Sl. No.	Place	Year of Installation	Capacity of the Plant, mil. cft/day	Raw Material Used	Gas Product
1. Oulu, Finland		1952	20	Now changed to oil	Hydrogen
2. Ouahama, Japan		1955	7.5-10	Coal	"
3. Puentes, Spain		1958	7.5-10	Lignite	"
4. Ptolemais, Greece		1959	20-25	Coal	"
5. Zandocrde, Belgium		1958	7.5-10	Now changed to Bunker oil	"
6. Estarreja, Portugal		1955	6	Now changed to oil	"
7. Mazingerbe, France		1955	7.5	Coal	"
8. Luoisana, U.S.A.		—	—	Abandoned	—
9. India				Coal	Hydrogen
10. Zambia				Coal	"

* Draft Report of Working Group No. 10 submitted to the Planning Commission, 1974.

(Note on the conversion of coal to industrial fuel gas and town gas by total gasification).

as the Neyveli plant is reported to be running at much below its rated capacity since its inception. Some of the commercial coal gasification plants based on Koppers-Totzek and Lurgi processes under operation throughout the world are mentioned in Tables 2 and 3 respectively. In India, the three proposed coal-based fertilizer plants at Ramagundam, Talcher and Korba, each having a capacity of 900 tonnes of ammonia per day, will be based on Koppers-Totzek process.

Pilot Plant Studies at CFRI on Complete Gasification of Coal

Down-draft Gasification Plant: A down-draft suspension gasification pilot plant with a 150 mm. diam. reactor, (Fig. 1) was installed in 1952 and operated with high, volatile pulverized coals (80 per cent through 200 mesh BS sieve) and oxygen-enriched air for production of fuel gas and synthesis gas. The relative disposition of coal dust burner and secondary air ports was so adjusted as to help in the production of a spread out reaction zone and this prevents slagging in the vicinity of the burner. The calorific value of the coal was 5961 K. cal/kg. and its caking index is less than 3. The results of proximate and ultimate analysis of the coal are as follows: *Proximate analysis* (per cent air-dried basis)—moisture 7.5, ash 14.1, volatile matter 33.9, and fixed carbon 44.5 per cent. *Ultimate analysis* (per cent air-dried basis)—moisture 7.50, mineral matter 15.48, carbon 62.15, hydrogen 4.17, nitrogen 1.46, sulphur 0.47, and oxygen (by diff.) 8.77

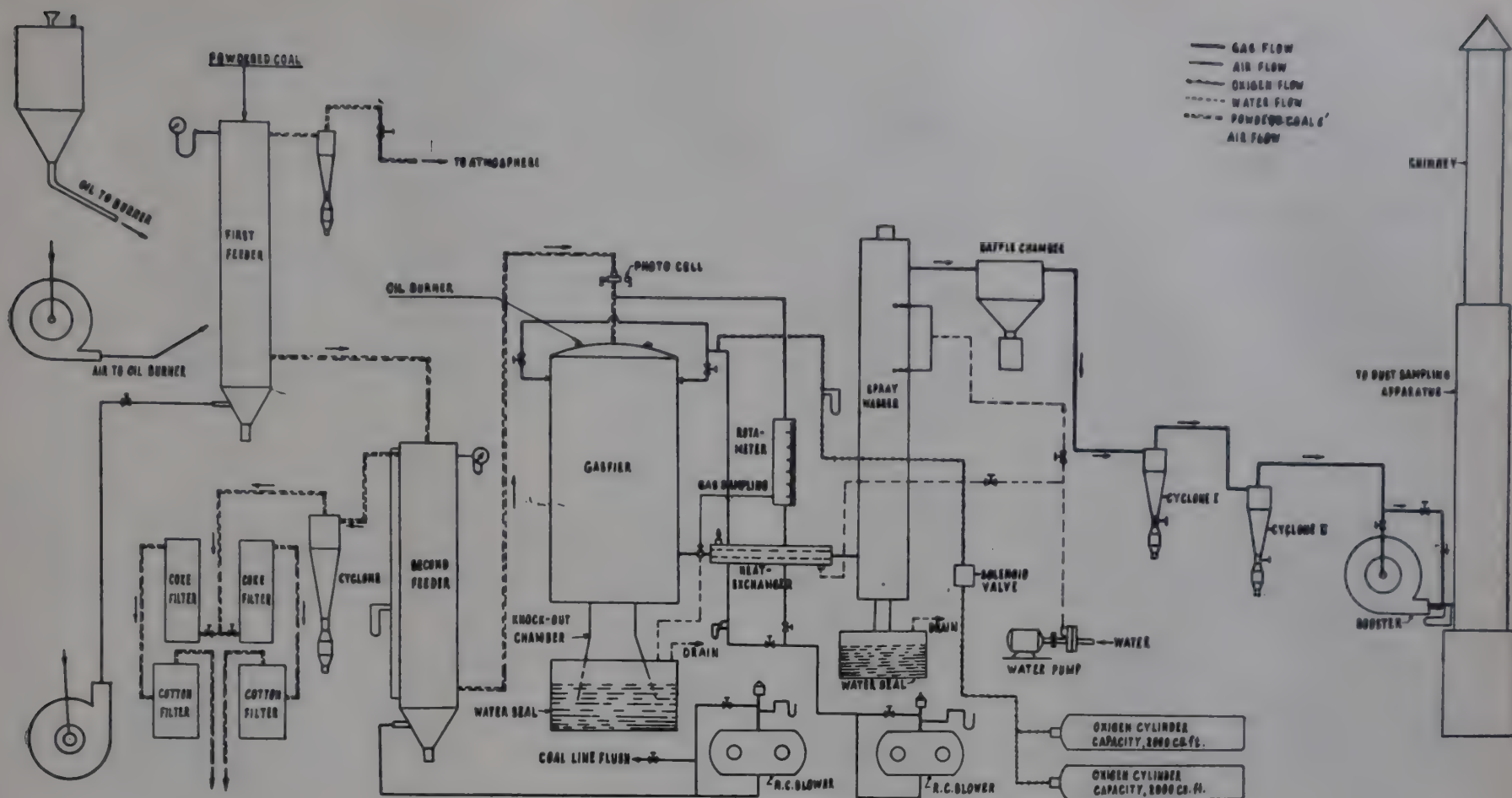


Fig. 1—Down-draft Gasification Pilot Plant (flowsheet)

per cent. The results of tests with a typical non-coking coal of Raniganj coalfield are presented in Table 4. It was seen that at 50 per cent oxygen-enrichment in the gasifying medium, a fuel gas of 1454 K.cal/Nm³ could be obtained with a carbon conversion efficiency around 50 per cent. For production of gas suitable for ammonia synthesis, the oxygen-enrichment of the gasifying medium has to be raised to about 70 per cent. Investigation with higher oxygen enrichments in the plant were, however, abandoned owing to lack of elaborate safety controls.

In the long duration runs, particularly with high oxygen-enrichment in the gasifying medium, considerable deposits were built up inside the gasifier, which gradually reduced the reactor volume. In such circumstances, it was necessary to clean the gasifier periodically.

Koppers-Totzek Pilot Plant

In view of the wide scope of the Koppers-Totzek type gasifiers in utilizing abundantly available low grade, undersized coals for production of synthesis gas, a pilot plant (Fig. 2) based on this process was put into operation in 1958. This plant has a capacity for gasifying 110 kg. of coals per hour and is complete with all necessary unit from preparation of coal up to the final cooling and cleaning of the synthesis gas.

The Buttner coal preparation unit prepares dust coal of the specified size and dryness which is conveyed pneumatically to the feed bin. The gasifier is a horizontal cylindrical shell of refractory brick-lining and has, unlike the commercial plants, one single coal burner placed at one of its ends while a gas burner for pre-heating rests on the other. A screw conveyor placed below the feed bin delivers the rated quantity of coal into a stream of oxygen passing through the burner. Steam can be admitted in the gasifier either through the oxygen line or through a jacket surrounding the coal burner. The hot gases emerging from the gasifier are treated in the gas cooling and dedusting sections before they are metered.

Gasification Characteristics of Lignite

(a) *Test with Neyveli Lignite* : The useful exploitation of large deposits of lignite at Neyveli assumed considerable importance and at the request of Neyveli Lignite Corporation, the gasification characteristics of this lignite were studied in the pilot plant to assess its suitability for synthesis gas manufacture in suspension gasification.

The moisture content of the raw material was about 55 per cent. Prior to conducting gasification tests, its moisture content was reduced to 4-8 per cent by hot flue gas drying in the ball mill of the coal preparation

TABLE 3—LURGI GASIFICATION PLANTS*

Sl. No.	Place	Year of Installation	Diam. of Gasifier and no. of Gasifier	Capacity, mil cft/d	Raw Material	Gas Product
1.	Hirschfelde, Central Germany	1936	3' 9" 2 nos.	1	Brown coal	Town gas
2.	Bohlen, Central Germany	1939	8' 6" 10 nos.	25	Brown coal	Town gas
3.	Brox, Czechoslovakia	1942	8' 6"	25	Brown coal	Town gas
4.	Sasolburg, South Africa	1955	12' 10" 10 nos.	150	Low grade coal	Synthesis gas CO+H ₂ for oil and chemicals
5.	Solihull, England experimental plant	1955	3' 9"		Low grade coal	Converted to slagging gasifier
6.	Dorsten, West Germany	1956	8' 6"	50-70	Weakly caking coal, now oil	Town gas
7.	Morwell Australia	1956	8' 6" 6 nos.	15	Brown coal	Town gas, plant shut-down
8.	Westfield, Scotland (UK)	1960	8' 6" 8 nos.	30-40	Low rank coal	Town gas
9.	Coleshill, England	1963	8' 6"	30-40	Low rank coal	Town gas
10.	Pakistan	1964	8' 6"	10	Low grade coal	Hydrogen
11.	North Korea	1965	8' 6"	20	Anthracite 45% ash	Hydrogen
12.	Uzin, Czechoslovakia	1965	N.A.	85	Brown coal	Town gas

* Draft Report of Working Group No. 10, Planning Commission, 1974. (Note on the conversion of coal to industrial fuel gas and town gas by total gasification).

TABLE 4—SOME TYPICAL RESULTS OF DOWN-DRAFT GASIFICATION PLANT

Feed Rate, kg./hr	Oxygen Enrichment, per cent	Oxygen/Coal Ratio, kg./kg.	Gas Composition, % by vol.					Exit Gas Temp., °C	Gas Produced, Nm ³ /hr
			CO	CO ₂	H ₂	O ₂	N ₂		
34.1	45	0.5	26.7	11.7	16.2	—	45.4	—	29.8
		0.6	30.0	9.7	17.4	—	43.6	—	38.0
		0.7	32.0	10.0	15.3	—	42.7	—	45.4
		0.8	26.4	15.6	15.2	0.6	42.2	945	51.2
27.3	45	0.5	25.7	14.8	12.9	—	46.6	—	23.7
		0.6	29.5	13.3	15.5	—	41.7	—	32.1
		0.7	30.4	12.3	14.9	—	42.4	—	36.4
		0.8	26.0	17.2	13.6	—	43.2	820	40.6
27.3	50	0.5	26.1	16.5	15.0	—	42.4	622	21.3
		0.6	28.4	15.6	17.7	—	38.3	560	28.2
		0.7	30.5	14.8	18.2	—	36.5	750	34.5
		0.8	29.7	15.3	15.8	—	39.2	820	36.6
22.7	50	0.5	23.0	14.0	16.3	0.7	46.0	660	16.4
		0.6	22.4	17.4	15.6	—	44.6	700	21.3
		0.7	27.6	12.8	14.1	—	45.5	700	23.2
		0.8	24.8	18.5	14.2	—	42.5	750	28.4
22.7	60	0.7	29.3	18.7	17.4	—	34.6	—	20.3

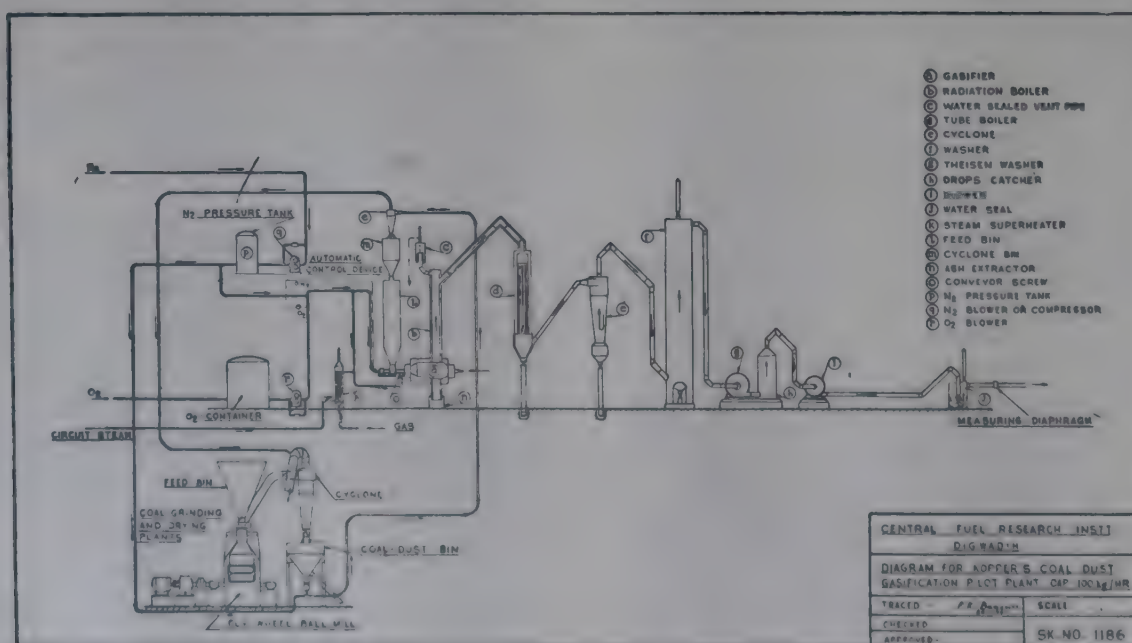


Fig. 2—Suspension Gasification Pilot Plant (flowsheet)

unit. The drying of lignite, being hazardous particularly in the powder state, necessitated incorporation of certain safety measures in the coal preparation unit. The different tests conducted were primarily aimed at determining the optimum operating conditions of the plant with lignite. The analysis of lignite samples and the results of tests carried out in the pilot plant under different oxygen/coal ratios ranging from 0.503 to 0.703 kg. per kg. are given in Table 5. In all tests, the lignite used was ground to a fineness of about 87 per cent through 200 mesh RS sieve. Fig. 3 shows the increase

of CO/H₂ ratio with the increase of oxygen/coal ratio and in Fig. 4 is shown the influence of oxygen/coal ratio on gasifier performance as judged by figures for gas production in Nm³/kg. of coal, per cent carbon gasified and per cent thermal efficiency. The percentage decomposition of steam for these experiments was found to lie between 50 and 54, presuming that the entire hydrogen in gas comes from decomposition of steam. From Table 5 it may be seen that by employing low oxygen/coal ratio, the requirement of oxygen for producing 1000 Nm³ of synthesis gas (CO + H₂) is low

TABLE 5—SUMMARY OF TEST RESULTS WITH NEYVELI LIGNITE

Sl. No.	Test Number							
	1	2	3	4	5	6	7	8
1. Coal Feed Rate (dry), kg./hr	103.5	111.3	111.3	111.3	111.3	111.3	111.3	103.0
2. Oxygen/Coal (dry) Nm ³ /kg.	0.3521	0.3890	0.4113	0.4113	0.4431	0.4431	0.4629	0.4926
3. Oxygen/Coal (dry), kg./kg.	0.503	0.556	0.587	0.587	0.633	0.633	0.661	0.703
4. Steam/Coal (dry), kg./kg.	0.239	0.212	0.212	0.253	0.212	0.269	0.253	0.220
5. Product Gas Composition, % by vol.								
CO ₂	14.8	13.4	14.3	15.2	13.4	15.4	15.0	13.8
CnHm	nil	nil	nil	nil	nil	nil	nil	nil
O ₂	0.4	0.2	nil	nil	nil	nil	0.2	0.2
CO	46.2	50.0	50.5	49.6	53.1	49.1	50.4	53.0
H ₂	31.9	32.3	31.5	33.0	31.5	32.7	31.2	29.1
CH ₄	2.5	1.1	1.0	0.6	0.2	0.4	0.5	0.9
N ₂	4.2	3.0	2.7	1.6	1.8	2.4	2.7	3.0
6. Calorific Value, K. cal./Nm ³	2614	2609	2590	2569	2593	2528	2531	2584
7. Carbon Monoxide/Hydrogen	1.45	1.55	1.60	1.50	1.69	1.50	1.62	1.82
8. Gas Produced/kg. of Coal (dry), Nm ³	1.345	1.442	1.437	1.442	1.499	1.502	1.519	1.526
9. Per cent Carbon Gasified	75.6	81.9	83.3	83.1	88.0	85.8	88.1	89.8
10. Per cent Thermal Efficiency	62.7	66.9	66.1	65.8	69.1	67.5	68.3	69.5
11. Requirement of Principal Raw Materials for Producing 1000 Nm ³ (CO+H ₂)								
Coal (dry), kg.	952.1	842.6	848.6	839.2	788.4	813.7	806.7	798.2
Coal (6% moist.), kg.	1013	896.4	902.8	893.0	838.7	865.8	858.2	849.2
Oxygen, Nm ³	335	328	349	345	349	361	374	393
12. Analysis of Coal Used, % by wt.								
Moisture	4.8	7.4	7.4	7.4	7.4	7.4	7.4	5.4
Ash	11.8	11.7	11.7	11.7	11.7	11.7	11.7	11.5
V.M.	44.7	46.2	46.2	46.2	46.2	46.2	46.2	46.2
Fixed Carbon	38.7	34.7	34.7	34.7	34.7	34.7	34.7	36.9
Carbon	57.56	56.33	56.33	56.33	56.33	56.33	56.33	58.23
Hydrogen	4.07	4.15	4.15	4.15	4.15	4.15	4.15	4.20
Sulphur	0.96	0.86	0.86	0.86	0.86	0.86	0.86	0.81
Nitrogen	0.86	0.60	0.60	0.60	0.60	0.60	0.60	0.60
13. Size of Coal, % through a 200 mesh (BSS)	88	87	87	87	87	87	87	86
14. Ash Fusion Range, °C								
Initial Deformation Temp.	Oxidizing atmosphere		1260	Reducing atmosphere		1250	—	—
Hemisphere Temp.	—		1280	—		1280	—	—
Fluid Temp.	—		1310	—		1290	—	—

but coal consumption is increased. On the other hand, when oxygen/coal ratio is high, consumption of coal is reduced for producing the same quantity of $(\text{CO} + \text{H}_2)$. The determination of the optimum operating conditions for economic synthesis gas production lies in selecting the conditions that will strike an economic balance between the cost of oxygen and coal. In spite of low ash fusion temperature of lignite tested, no major deposit built-up trouble in the gasifier was experienced. The test conducted have established favourable technical possibilities for adopting suspension gasification technique for producing synthesis gas from Neyveli lignite.

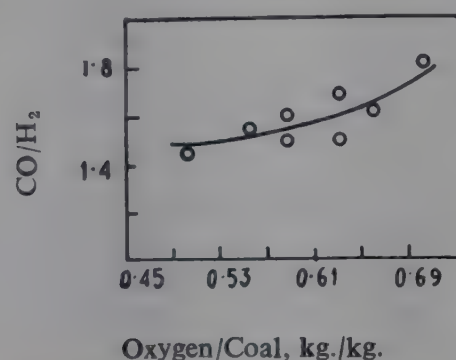


Fig. 3—Variation of CO/H_2 Ratio with Oxygen/Coal Ratio (Neyveli Lignite)

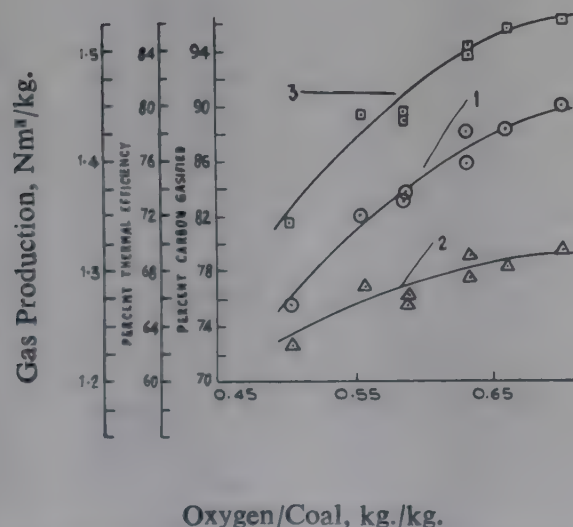


Fig. 4—Effect of Oxygen/Coal Ratio on Gas Yield, Thermal Efficiency and Carbon Gasified.

1. Carbon Gasified % 2. Thermal Efficiency %
3. Gas Produced.

(b) *Test with Kutch Lignite* : At the request of Gujarat Mineral Development Corporation, similar tests with Kutch lignite were conducted. Based on the consumption figures obtained in the pilot plant under optimum operating conditions, consumption figures for a full-scale commercial plant designed to supply necessary synthesis gas for a projected 600 tpd ammonia plant have been calculated (Table 6).

TABLE 6—PRODUCTION & CONSUMPTION FIGURES FOR SYNTHESIS GAS PLANT

(Capacity: Equivalent to 600 tpd ammonia)

	Per day
1. <i>Consumption</i>	
Coal dust (dry), tonne	1090
Oxygen, Nm^3	500×10^3
Steam, 2.5 atmospheres (b), tonne	165
Power (a), Kw.hr.	65.1×10^3
Water (make-up) (b), M^3	4500
2. <i>Production</i>	
Raw Synthesis gas, Nm^3	1.55×10^6
$(\text{CO} + \text{H}_2)$ in Synthesis, Nm^3	1.29×10^6
Steam at 5 atmospheres, tonne	1090
Carbon dioxide gas (c), Nm^3	0.92×10^6
3. <i>Requirement of Pure Carbon Dioxide Gas (stoichiometric) for Urea Production</i>	0.396×10^5

Note: a. Requirement of coal for drying not included.
b. Based on commercial plant data.
c. Presuming 95% recovery of total CO_2 formed during gasification and gas purification.

Gasification Characteristics of Bituminous Coal

Several pilot plant tests were carried out with non-caking bituminous coals from different coalfields. The coals tested included Jambad Bowlah, Lower Kenda, Talcher, Singrauli, Umrer and Argada. The performance data obtained with typical non-cooking coals of Raniganj coalfield are discussed here to focus the broad characteristics of non-caking bituminous coals in suspension gasification with steam and oxygen. The proximate and ultimate analysis and heating values of two such coals samples as well as their ash fusion characteristics are given in Table 7. Since the moisture content of the coals was only about 5 per cent, no drying prior to gasification was necessary.

In the first of two series of tests conducted, the performance of gasifier was studied at oxygen-coal ratios in the range 0.58-0.85 kg./kg. at two different levels of steam-coal ratios. These tests were subdivided into two categories depending on the steam-coal ratio used and also on the technique adopted for adding steam to the gasifier. In the first category, steam-coal ratios around 0.15 (0.08-0.21) were used and the steam was blended with oxygen prior to its entry into the gasifier.

In the second category, steam-coal ratios around 0.35 (0.30-0.40) were employed by admitting the steam through the jacket surrounding the coal burner. In the second series of tests, different quantities of steam were admitted through the jacket while keeping the coal feed rate and oxygen flow to the gasifier same in all the

TABLE 7—ANALYSIS AND OTHER CHARACTERISTICS
OF COAL SAMPLES USED

	Sample A	Sample B
Proximate Analysis, per cent		
Moisture	5.7	4.3
Ash	15.6	16.9
Volatile matter	35.4	34.5
Fixed carbon	43.3	44.3
	100.0	100.0
Ultimate analysis, per cent		
Moisture	5.70	4.30
Mineral matter	17.16	18.59
Carbon	63.20	64.82
Hydrogen	4.56	4.38
Sulphur	0.37	0.49
Nitrogen	1.52	1.79
Oxygen	7.49	5.63
	100.00	100.00
Heating value (gross), K.cal./kg.	6153	6316
Ash fusion range		
Initial deformation temp., °C	1170	1160
Hemisphere temp., °C	>1400	>1400

tests. The results of gasification for the three sets of experiments are presented in Table 8. In the first series, (CO+H₂) percentage, CO/H₂ ratio in the product gas, per cent carbon gasified, per cent thermal efficiency and gas yield have been plotted against oxygen/coal ratio (Figs 5-8). In the second series, the variation of all the above five parameters and also the CO₂ percentage in the raw gas with steam-coal ratio are shown in Figs. 9 and 10.

The cost of oxygen is considered to be a major factor in the economics of production of synthesis gas. For an approximate guide the cost of 1 kg. of coal may be taken as equivalent to the cost of 0.5906 Nm³ of oxygen and on this basis an economic factor has been calculated to define the best compromise. The economic

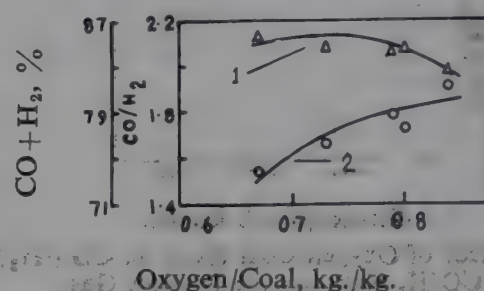


Fig. 5—Effect of O₂/Coal Ratio on CO+H₂% and CO/H₂ Ratio in the Product Gas (Steam through Oxygen Line)
1. CO+H₂ % 2. CO/H₂

TABLE 8—RESULTS OF GASIFICATION TESTS WITH RANIGANJ COAL (KOPPERS-TOTZEK PROCESS)

Coal Feed Rate, kg./hr.	Oxygen Coal Ratio, kg./kg.	Steam/ Coal Ratio, kg./kg.	Product Gas Composition, % by vol.					Gasifier Outlet Temp., °C	Gas Production of Coal, Nm ³ /kg. of coal	Cal.val. (gross), K.cal./ Nm ³	Carbon Gasified, %	Thermal Effi- ciency, (gross), %	Raw Materials for Producing 1000 Nm ³ (CO+H ₂)		
			CO ₂	CO	H ₂	CH ₄	N ₂						Coal* kg.	O ₂ Nm ³	
1. Coal Sample B: Steam through Oxygen Line															
90.46	0.67	0.21	11.5	52.2	33.7	0.2	2.4	1095	1.371	2632	72.4	57.3	850.0	398	
89.10	0.73	0.14	11.8	53.2	31.9	nil	3.1	1080	1.524	2589	81.9	62.6	772.1	394	
82.73	0.79	0.08	12.9	54.6	30.2	nil	2.3	1070	1.553	2579	86.7	63.7	758.6	419	
80.91	0.80	0.16	12.5	54.2	31.0	0.2	2.1	1110	1.547	2611	85.6	64.1	758.6	424	
77.27	0.84	0.15	13.2	54.7	28.4	0.3	3.4	1115	1.565	2557	88.3	63.5	768.8	451	
2. Coal Sample A: Steam through Jacket															
100.00	0.58	0.36	18.1	38.1	39.8	2.3	1.7	1040	1.335	2592	66.3	56.4	961.6	390	
100.90	0.67	0.30	14.6	49.8	32.9	0.4	2.3	1095	1.388	2555	76.3	57.8	872.0	409	
93.64	0.68	0.33	15.2	50.3	32.9	0.2	1.4	1110	1.382	2552	77.0	57.5	870.4	414	
90.46	0.73	0.40	16.6	46.3	34.4	0.6	2.1	1070	1.541	2514	83.1	63.1	804.1	410	
78.17	0.85	0.35	17.9	47.7	31.1	0.4	2.9	1130	1.618	2435	90.6	64.2	784.0	466	
3. Coal Sample A: Steam through Jacket; Coal Feed Rate and Oxygen-Coal Ratio Constant															
93.64	0.68	0.26	12.0	52.2	32.3	nil	3.5	1100	1.394	2573	75.9	58.4	848.1	403	
93.64	0.68	0.33	15.2	50.3	32.9	0.2	1.4	1110	1.382	2552	77.0	57.5	870.4	414	
93.64	0.68	0.38	16.8	47.7	33.5	0.1	1.9	—	1.418	2480	77.7	57.3	868.5	413	
93.64	0.68	0.47	17.1	48.0	33.4	0.1	1.4	—	1.352	2486	74.8	54.8	909.2	432	

* on air-dried basis

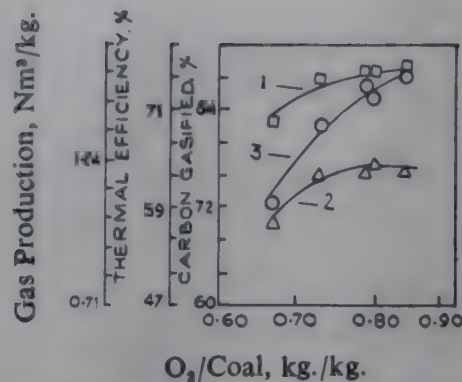


Fig. 6—Effect of Oxygen/Coal Ratio on Gas Yield, Thermal Efficiency and Carbon Gasified [Steam through Oxygen Line]
Legend
1. Gas Yield 2. Thermal Efficiency 3. Carbon Gasified

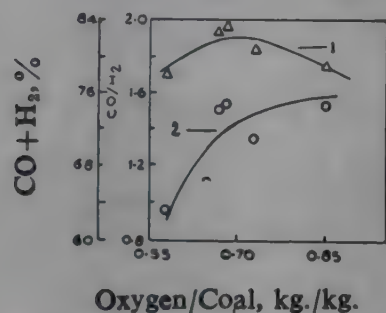


Fig. 7—Effect of Oxygen/Coal Ratio on CO+H₂% and CO/H₂ Ratio on the Product Gas [Steam through Jacket]
Legend
1. CO+H₂% 2. CO/H₂ Ratio

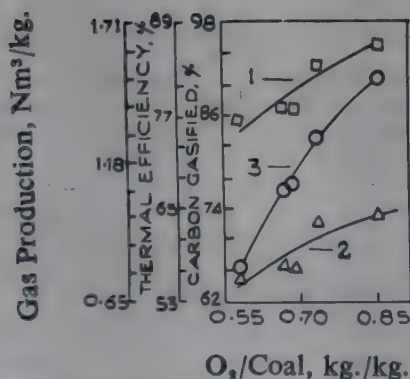


Fig. 8—Effect of Oxygen/Coal Ratio On Gas Yield, Thermal Efficiency and Carbon Gasified [Steam Through Jacket]
1. Gas Yield 2. Thermal Efficiency 3. Carbon Gasified

factor is stated in terms of coal per 1000 Nm³ of (H₂+CO) in the synthesis gas. The plots of economic factor against oxygen-coal ratio for the two sets of experiments of the first series are shown in Fig. 11. At the minimum economic factor, the figures for carbon conversion and thermal efficiencies for the pilot plant are about 82 and 63 per cent respectively. The carbon efficiency and thermal efficiency (net) of commercial plants of dry ash bottom type are nearly 89 and 67 per cent respectively with recycling of high carbon rejects of cyclone separator. No provision, however, exists in

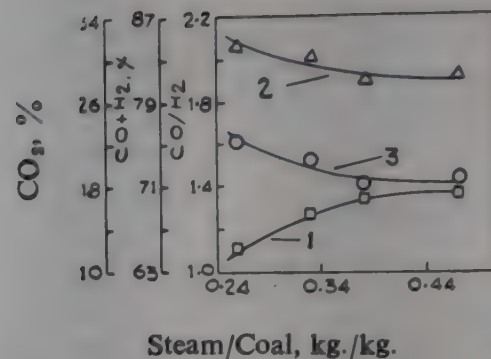


Fig. 9—Effect of Steam/Coal Ratio on CO₂%, CO+H₂ and CO/H₂ Ratio in the Product Gas [Steam through Jacket]
Legend
1. CO₂% 2. CO+H₂% 3. CO/H₂ Ratio

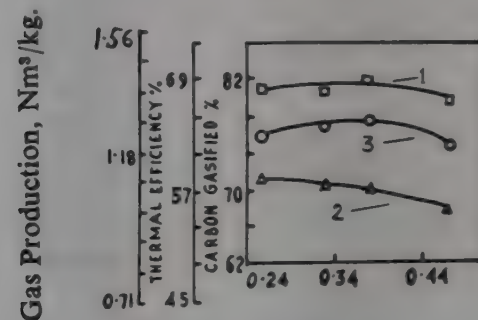


Fig. 10—Effect of Steam/Coal Ratio on Gas Yield (1), Thermal Efficiency (2) and Carbon Gasified (3)

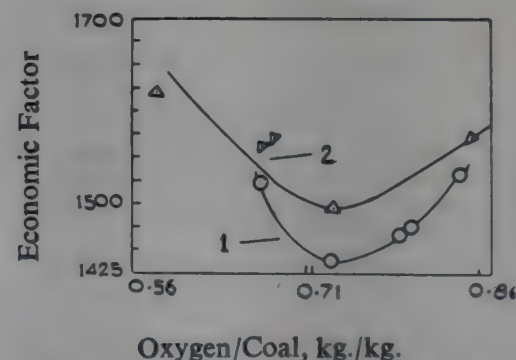


Fig. 11—Effect of Oxygen/Coal Ratio on the Value of the Economic Factor
1. Steam through Oxygen Line 2. Steam through Jacket

the pilot plant for the collection and recycling of high carbon rejects but if adopted, this should further improve the plant efficiency.

The steam-coal ratio (around 0.15) employed in the first set of experiments appears to be optimum for the coal feed rates tested, but an increased throughput of coal with consequent lower heat losses from the gasifier for every kg. of coal gasified will bring about a rise in the gasifier temperature and this will possibly necessitate a higher proportion of steam-coal ratio in maintaining a suitable temperature for preventing clinkering inside the gasifier. A part of the steam should preferably be added through the jacket surrounding the coal burner

as this will ensure, apart from other things, a longer life of the refractory lining of the gasifier. Increased throughput of coal means higher gas velocity for the suspended particles and as a result the extent of deposit formation will be less.

The gasification characteristics of non-caking coals of Madhya Pradesh and Orissa coalfields were of same nature as found with the Raniganj coals with regard to gas quality, thermal efficiency and percent carbon gasified, etc. The only significant difference noted was that the low hydrogen (subhydrous) coals of Madhya Pradesh coalfields consumed 20-50 vol. more oxygen while the less matured coals of Orissa consumed 10-30 vol. less oxygen compared to those for Raniganj coals for production of 1000 vol. of $(\text{CO} + \text{H}_2)$. It was also observed that high ash middlings of Argada coals containing about 32 per cent ash consumed about 475-508 vol. of oxygen per 1000 vol. of $(\text{CO} + \text{H}_2)$ produced.

To study the influence of ash on gasification performance, tests were carried out with Argada cleans, blends of Argada cleans and middlings and Argada middlings only. The variation against oxygen-coal ratio, of per cent carbon gasified, per cent thermal efficiency, coal (d.a.f. basis) and oxygen requirement for production of 1000 Nm^3 of $(\text{CO} + \text{H}_2)$ are presented in Figs. 12-15.

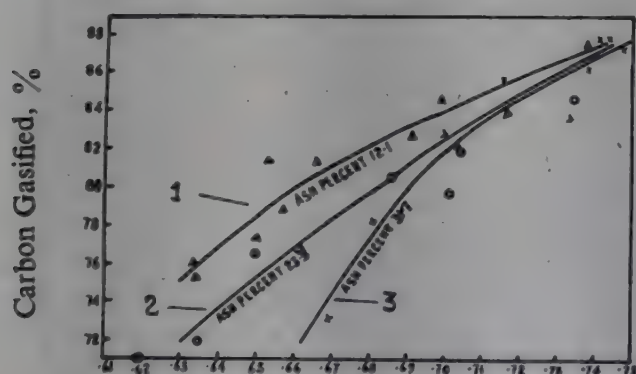


Fig. 12—Variation of Per cent Carbon Gasified with Oxygen/Coal (d.a.f.) Ratios for Argada Coals of Varying Ash Content

1. Clean. 2. Clean + Middlings. 3. Middlings

The results clearly show the beneficial effects of using low ash coals for gasification. At the lowest ash content of the feedstock, the figures for gasification performance as judged by per cent carbon gasified, per cent thermal efficiency, volume of oxygen and d.a.f. coal requirement per 1000 vol. of $(\text{CO} + \text{H}_2)$ produced show best results. Although there is some overlapping of results between those of blend of middlings and clean

and those of middlings alone, but when the two are compared against clean coal the benefits of using low ash coals are quite wide and well defined.

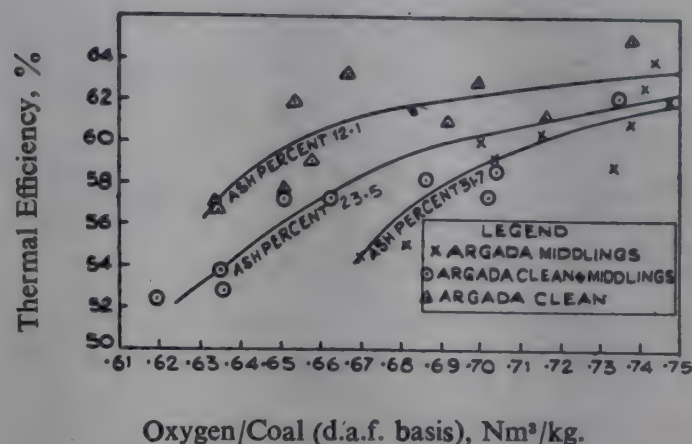


Fig. 13—Variation of Thermal Efficiency with Oxygen/Coal (d.a.f. basis) Ratios for Argada Coals of Varying Ash Content

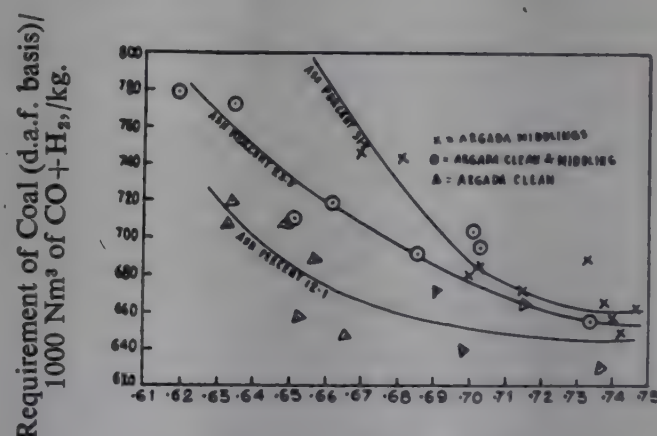


Fig. 14—Varying Coal Requirement with Oxygen/Coal Ratio for Argada Coals of Varying Ash Content

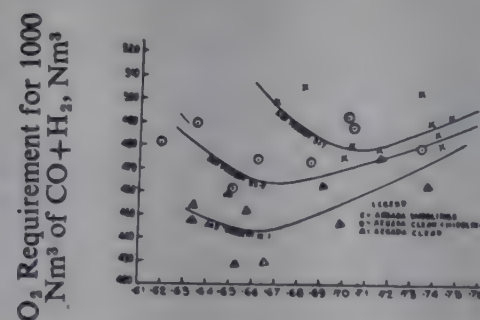
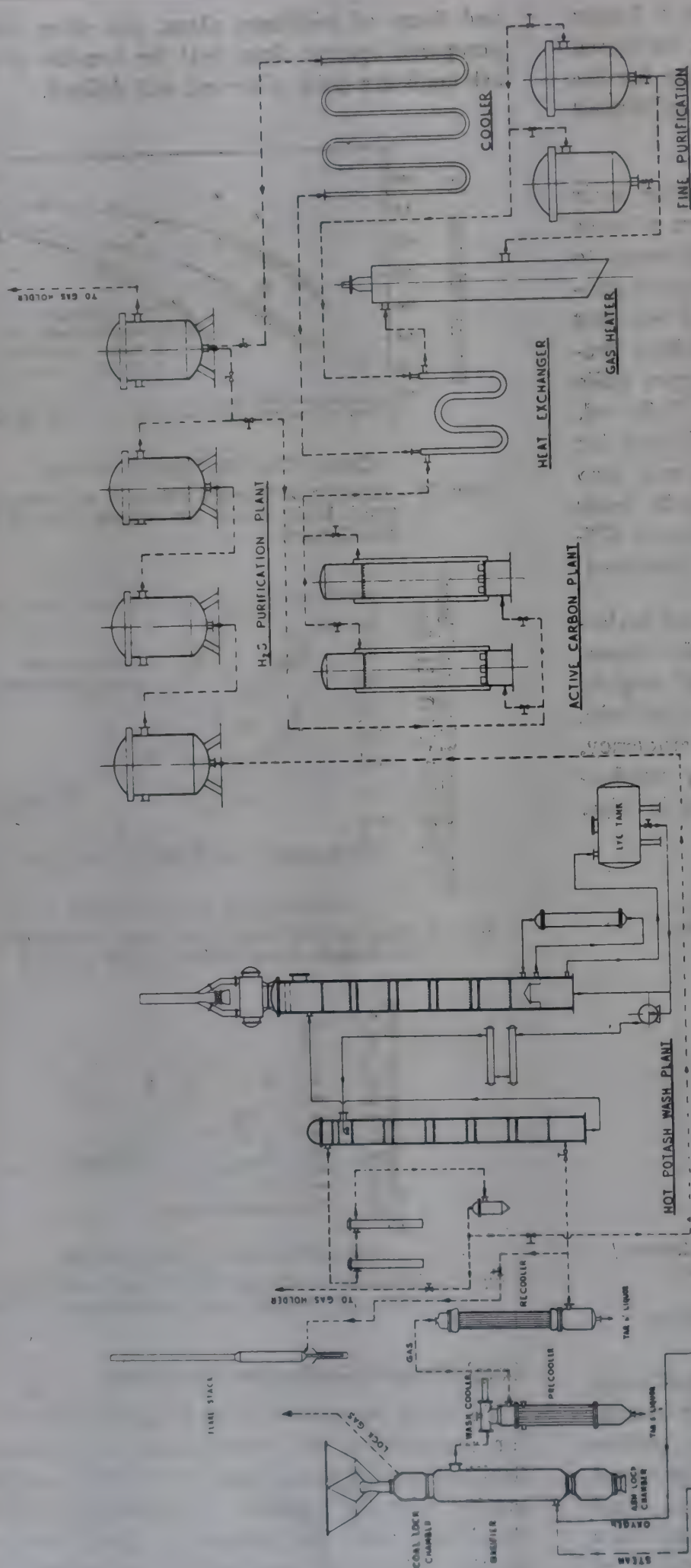


Fig. 15—Variation of Oxygen Requirement with Oxygen/Coal Ratios for Argada Coals of Varying Ash Contents

Lurgi Pressure Gasification Pilot Plant

To study the potentialities of gasification technique for manufacture of synthesis gas for production of fertilizers and chemicals and its possible economic integration with the synthetic oil industry as well as for developing town gas industry, a Lurgi pressure gasification pilot plant was installed and commissioned at CFRI in 1962.



FLOW DIAGRAM FOR **LURGI PRESSURE GASIFICATION PILOT PLANT** WITH **LINDE OXYGEN PLANT & BORSIG BOILER** **C.F. R.I.**

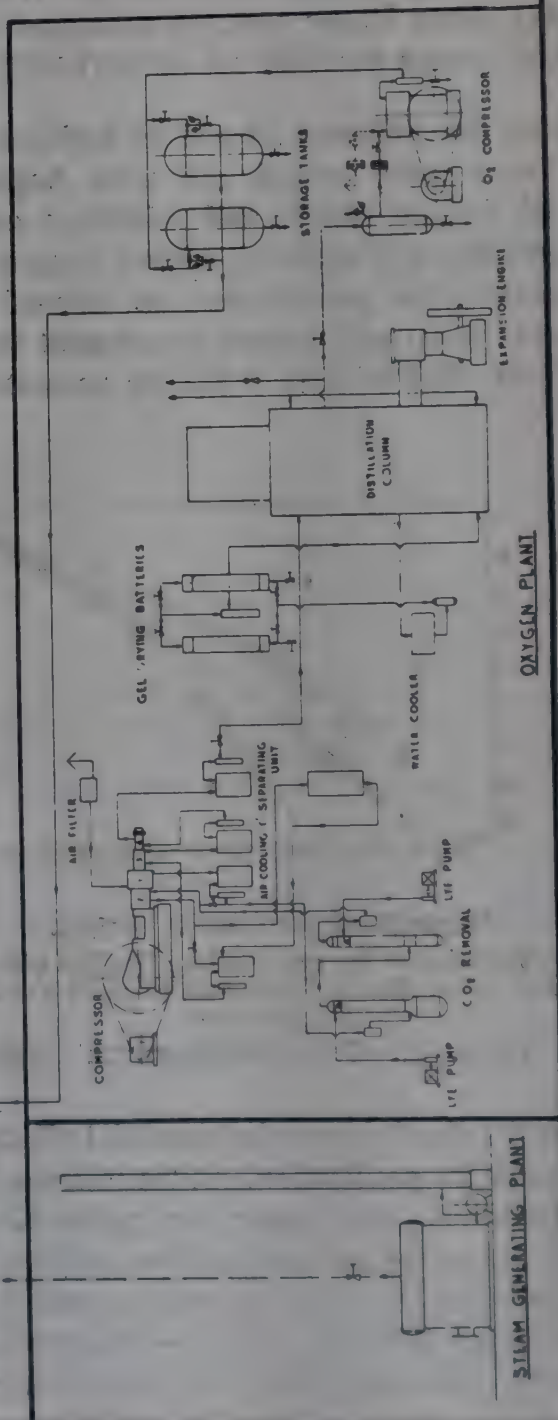


Fig. 16

The pilot plant was designed to gasify 0.8 tonne of coal per hour to produce 1400 NmC³ of raw gas at a pressure of 32 kg. per sq. cm. For supplying necessary steam and oxygen to the gasifier, the plant is equipped with a boiler and oxygen plant. A general flowsheet of the plant is presented in Fig. 16.

The hot gases emerging out of the gasifier are first subjected to direct cooling to remove bulk of the tar and then passed through subsequent coolers, carbon dioxide removal and fine purification systems.

Experimental Work : A number of tests with non-caking bituminous coals from W. Bengal, Orissa, Madhya Pradesh and Andhra Pradesh coalfields were undertaken. Performance data obtained with four typical non-caking coals, viz. Dobrana, Talcher, Burhar and Singareni, from the above coalfields are discussed.

The data on proximate and ultimate analyses, caking index, calorific value and ash fusion characteristics of these coals are given in Table 9 while the results of gasification tests under different operating conditions are given in Table 10. All these tests using 6-25 mm. coals were carried out at four levels of pressures and the plots of the methane content, calorific value of raw gas, per cent carbon gasified and per cent thermal efficiency against gasifier pressure are presented in Figs. 17-20. During studying the influence of gasifier pressure on the above four parameters, the steam-oxygen ratio varied within close limits for the individual coals tested. With nearly the same steam-oxygen ratio an increase in gasifier pressure increases the rate of reactions inside the gasifier, thereby increasing the coal input on unit gasifier cross-section per hour. An increase in the coal feed rate to the gasifier helps to minimize the heat losses per unit weight of fuel charged and this in turn helps in bringing about improvements in conversion efficiencies. These basic facts are supported by test results barring only a few instances.

The concentrations of hydrogen sulphide ammonia nitric oxide and benzene in the tar scrubbed gas were determined for different coals tested. The concentration of hydrogen sulphide (g./100 Nm³ gas) was found to vary from 366 to 538 for Talcher coal, from 252 to 294 for Singareni, from 275 to 336 for Dobrana and from 292 to 304 for Burhar coal. The concentration of ammonia expressed as g./100 Nm³ of gas varied from 12 to 14 for Talcher coal from 15 to 22 for Singareni, from 18 to 50 for Dobrana and from 10 to 32 for Burhar coal. The concentration of nitrogen oxide in the gas was found to be about 0.3 ppm. for both Talcher and Singareni coals. The concentration of benzene in a

TABLE 9—CHARACTERISTICS OF COALS

	Talcher Coal	Singareni Coal	Dobrana Coal	Burhar Coal
<i>Proximate Analysis, %</i>				
Moisture	6.9	8.9	3.0	7.1
Ash	12.4	15.4	19.4	21.5
Volatile matter	35.6	26.3	32.5	28.2
Fixed Carbon	45.1	49.4	45.1	43.2
<i>Ultimate Analysis, % (air-dried basis)</i>				
Moisture	6.9	8.9	3.0	7.1
Mineral Matter	13.64	16.94	21.34	23.65
Carbon	65.69	60.84	61.83	57.49
Hydrogen	4.46	3.64	4.39	3.70
Sulphur	0.55	0.38	0.46	0.48
Nitrogen	1.39	1.46	1.84	1.56
Oxygen (by diff.)	7.37	7.84	7.14	6.02
<i>Calorific Value (gross), K.cal./kg.</i>				
	6494	5766	6067	5494
<i>Caking Index (BS)</i>				
	<5	<5	<5	<5
<i>Ash Fusion Range, °C (in mildly reducing atmosphere)</i>				
Initial Deformation Temp.	1140	1390	1100	>1400
Hemispherical Temp.	>1400	>1400	>1400	—

sample of the gas obtained from Singareni coal was found to be 637 ml./100 Nm³ of gas. The quality of tar obtainable from pressure gasification pilot plant and the relevant data concerning the distillation characteristics of Talcher tar are presented in Table 11. About 90 per cent of the total tar yield was light tar.

In the event it is desired to increase the synthesis gas yield *in lieu* of tar, this can be achieved by recycling back heavy tar to the gasifier and reforming the light tar with crude gas in a reformer.

Dobrana Coal Steam/O₂, 6.1-6.2 kg./Nm³

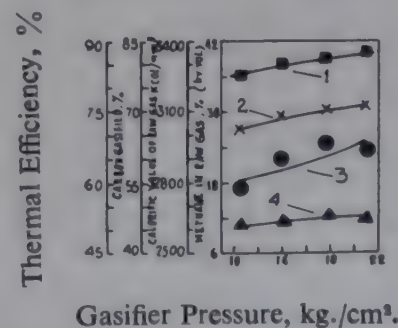


Fig. 17—Variation with Gasifier Pressure of Percentage of Methane in Raw Gas, Calorific Value of Raw Gas, Percentage Carbon Gasified and Thermal Efficiency for Dobrana Coal

1. Carbon Gasified
2. Thermal Efficiency
3. Calorific Value
4. Methane

[illegible]

The investigations carried out have established the amenability of Indian coals to pressure gasification and in spite of low initial deformation temperature of ash of some of the coals, no operational difficulty was encountered. From the correlations established between

Talcher Coal: Steam/Oxygen, 6.2-6.5 kg/Nm³

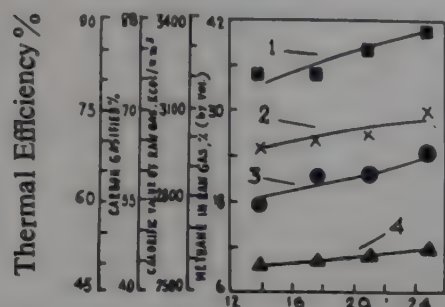


Fig. 18—Variation with Gasifier Pressure of Percentage of Methane in Raw Gas, Calorific Value, Percentage Carbon Gasified and Thermal Efficiency for Talcher Coal

Legend

1. Carbon Gasified
2. Thermal Efficiency
3. Calorific Value
4. Methane in Raw Gas

Burhar Coal: Steam/Oxygen, 5.9 to 6.1 kg./Nm³

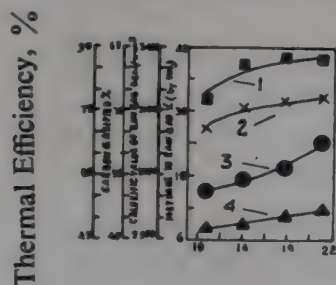


Fig. 19—Variation with Gasifier Pressure of Percentage of Methane in Raw Gas, Calorific Value of Raw Gas, % Carbon Gasified and Thermal Efficiency for Burhar Coal.

Legend

1. Carbon Gasified
2. Thermal Efficiency
3. Calorific Value
4. Methane in Raw Gas

Singareni Coal: Steam/O₂, 5.7-6.0 kg/Nm³

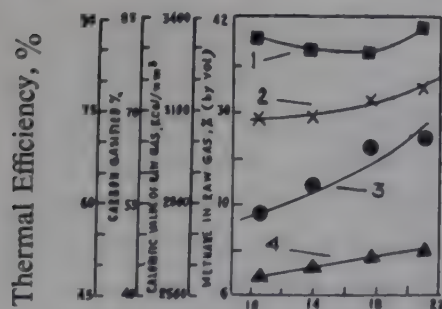


Fig. 20—Variation with Gasifier Pressure of Percentage of Methane in Raw Gas, Calorific Value of Raw Gas, Thermal Efficiency and Percentage Carbon Gasified for Singareni Coal.

Legend

1. Carbon Gasified
2. Thermal Efficiency
3. Calorific Value
4. Methane in Raw Gas

TABLE 11—ANALYSIS OF TALCHER TAR OBTAINED FROM HIGH PRESSURE COAL GASIFICATION PILOT PLANT

	Light Tar	Heavy Tar
Sp. Gravity at 29°C	0.9922	1.015
Water Content, % (vol./wt.)	1.4	1.96
Insoluble Matter in Benzole (up to 110°C), % of dry tar	0.3143	0.4611
Distillation Characteristics, % (Wt./wt. on dry tar) upto 170°C	0.85	nil
170-210°C	7.36	0.67
210-230°C	8.63	1.97
230-270°C	15.91	12.85
270-300°C	8.90	4.33
300-330°C	9.53	13.10
330-360°C	15.40	30.44
Total oils upto 360°C	66.78	63.36
Residue at 360°C	32.00	34.96
Distillation loss	1.22	1.68
Softening Point (R & B) of Residue at 360°C	55°C	73°C
Tar Acids, % (on dry tar) in upto 270°C fraction	5.39	4.71
In 270-300 °C fraction	5.23	9.84
Total	10.62	14.55
Tar Bases, % (on dry tar)		
In upto 270°C fraction	1.15	0.71
In 270-360 °C fraction	1.23	1.61
	2.38	2.32

plant pressure and gasifier performance, it would now be possible to predict, with a fair degree of accuracy, the expected performance figures of even untried fuels under a set of known operating conditions.

Identification of the Types of Coal and Techniques

The conventional coal gasification techniques have reached such a perfection that any fuel irrespective of its size or quality can be converted into synthesis gas. All that is required is a proper matching of the size of the fuel and its quality with the technique of gasification chosen. Fuels with low ash fusion point are preferred in slagging operation, whereas fuels should have a high ash fusion point if dry bottom operation is desired. Operation under pressure offers several advantages over systems operating at atmospheric pressure. From the view points of gasification convenience and efficiency, all the processes favour a fuel with low inert content and good reactivity. The non-conventional methods of gasification offer scope for reducing the cost of coal-based ammonia and several of these techniques are being studied to eliminate the need for costly oxygen.

These techniques, therefore, assume greater importance and have to be vigorously pursued.

Information on oxygen-fed Winkler's generators is rather unhappy even with a reactive fuel like Neyveli lignite. The only alternative therefore lies between the Koppers-Totzek and Lurgi processes for commercial production synthesis gas.

The pilot plant studies with Koppers-Totzek process have shown that any coal from lignite to high ash (32 per cent) washery middlings can be gasified but the oxygen consumption would be higher with high ash and less reactive fuels. The process, however, needs powdered coal and in the context of severe erosion problems being encountered in the pulverizer sections of the country's power stations a careful choice of coal and milling equipment is warranted.

In general, ash content is not only high in the Indian coals, but its quantity and quality are also quite inconsistent. Feed of consistent quality is very essential to ensure high level of efficiency for gasifiers and the installation of a simple jig along with gasification unit or at the colliery end might be beneficial. Although the ash of Indian coals is generally refractory in nature, a good majority of coals of Bengal-Bihar coalfields, in particular, has initial ash deformation temperature around 1100-1150°C and therefore efforts were made to operate the gasifier under dry bottom conditions allowing 70-80 per cent of the ash to escape with the gases. Nevertheless, layers of slags of varying depths were noted inside the gasifier in many of the tests. By doping the fuel with lime and operating with low steam/coal ratio, as has been proposed for the projected fertilizer plants, greater portion (say 40-50 per cent) of the ash can be melted out of the gasifier and it is expected that such a procedure would help in maintaining the continuity of operation without slag build-up troubles and stoppages. Only full-scale tests of long duration can help in ascertaining the true nature of the problem of deposit formation inside gasifier and performances of the projected plants on this issue would be noted with interest. Doping with lime for high ash coals would, however, affect adversely the thermal efficiency and oxygen consumption figures. The Koppers have lately designed high capacity gasifiers and the projected fertilizer plants in India based on Koppers-Totzek process will have gasifiers, each capable of generating synthesis gas sufficient for production of 300 tonnes/day of ammonia.

Pilot plant studies carried out with typical non-caking coals of different coalfields have established that claims for commercial Lurgi gasifiers can also be realized in practice with Indian coals. Although coals with 15-20 per cent ash and caking index around 5 or below were tested in the CFRI pilot plant, it is reported that coals up to 30 per cent ash and caking index up to 10 can be used in fixed bed pressure gasification plants. A high ash fusion point of coal is desirable and most of the bituminous coals of the country have high ash fusion point. The most important for this process is that it can take only sized fuels. Roughly the requirements of coal for gasification and steam generation are in the ratio of 75 : 25. Hence, a ready avenue for disposal of the excess fines from coal for other purposes has to be found out.

In India, where coals will normally have a high ash content, close sizing of coals in large quantities present special problem. A process which can use a solid heat-carrier in place of oxygen heating may be more attractive. It has been reported that the Union Carbide, in collaboration with Office of Coal Research (USA), are setting up a pilot plant in which agglomerated coal ash produced at the combustion stage for generation of steam will be recirculated as a heat-carrier for the initial steam gasification stage. At CFRI, a similar process is being considered where steam will be generated by combustion of char in a fluidized bed, the resulting ash will be fed to the gasifier for effecting steam-carbon reaction. The major advantage of this type of process will lie in elimination of costly oxygen plant by utilizing sensible heat of the ash, thus turning the handicap to an asset. Such a process will be particularly suitable for the low grade high ash Indian coals.

Conclusion

Coal, being a cheaper raw material compared to petroleum, merits consideration as feedstock for gasification and ultimately for the production of fertilizers. The extra cost involved in processing coal to ammonia will be compensated by the saving accrued from the economy of use of a cheaper rawmaterial. Much technological advances already made and being made, lend support to minimizing the cost of coal-based ammonia production. The development of non-conventional approaches of coal gasification without the use oxygen hold further promise for economic coal-based ammonia production. These methods not only call for a thorough examination for their feasibility but also require sincere follow-up for their commercialization. If coal has to compete with petroleum feedstocks for

fertilizer production, it is imperative that low ash coals should be used for synthesis gas generation. It follows, therefore, that high ash coals should be beneficiated prior to gasification for utilizing low ash coal for gasification and high ash fraction for power generation. Owing to the present oil crisis, coal is receiving due attention as a strategic raw material for fertilizer production in the development plans of the country.

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The current status of technology in respect of coal-based ammonia plants has been reviewed. The two main processes under commercial exploitation, viz. Lurgi and Koppers-Totzek processes, are compared. Some of the likely problems one might encounter with coal-based ammonia plants have been highlighted which should be taken note of in designing future plants in India. It has also been suggested that the commissioning date of at least one of the 3 coal-based plants under construction in India should be brought forward with a view to utilizing its operational experience in designing future plants.

Ammonia by Coal Gasification—Factors for Consideration in the Design of Future Plants for India*

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Case for Coal

Recent developments in the world petroleum situation have brought about a *volte face* in the crude importing countries with regard to the hitherto mounting, almost uncontrolled use of 'clean' fuels and feedstocks. To India, with her pressing food and foreign exchange problems, a fresh look at coal as an alternative source of hydrogen for ammonia production has become a compelling necessity of tactical, if not of strategic, importance. While development of ecologically more desirable energy sources should be actively pursued, the exploitation of India's vast reserves of bituminous coal to ease the fertilizer situation, at least in the medium term, is a course of action that today is almost self-evident. The Fertilizer Corporation of India's boldness and foresight in taking the decision to put up three large coal-based plants are highly commendable in this connection.

Much has been written on the comparative economies of coal-based ammonia production. With the fast pace of change in world prices of commodities and services, however apart from serious inflationary trends within the country, any economic appraisal made today is out of date almost by the time it goes to print. Economic comparisons, moreover, are not universally applicable, varying as they would, with the scope and

definition of the project, for instance, with respect to flexibilities and margins in design, prospects of diversification at the same site using same sources of feedstock and energy, extent of infrastructural provisions and the quantum of spending required on utilities, like water, power, effluent disposal, etc.

Suffice it to say, the coal-based fertilizer plants are expensive, almost unbearably so. With this proviso, it is evident that one of the principal factors that would decide the economic viability of these plants is their availability or capacity utilization, quantified by their ability to produce the annual tonnage as stipulated in design. The object of this paper is to highlight some of the likely problems one might encounter with coal-based ammonia plants and to evolve a 'check list' for consideration in designing future plants for India.

Status of Technology

The hydrogen content of coal is a meagre 1-5 per cent compared to a range of 10-25 per cent in petroleum feedstocks from heavy fuel oil to natural gas. Hydrogen production from coal has, therefore, to depend heavily on the generation of carbon monoxide and hydrogen by reaction of carbon in coal with steam and oxygen followed by the water gas shift reaction which liberates a mole of hydrogen for each mole of carbon monoxide. The overall reaction is endothermic, and equilibrium composition of the product gas depends principally on the temperature of gasification. With the present state of technology, reaction heat supply by internal combus-

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tion of part of the coal (partial oxidation) is still the only route followed in commercial plants.

In the earlier generation of coal-based plants like Sindri, gasification was achieved by an alternation of water gas and producer gas reactions in a fixed bed of coke. Use of coke eliminated the formation of devolatilization products of coal, but the overall thermal efficiency of the process was low, total consumption of fuel and energy per tonne of ammonia made (about 18×10^6 K. cal/te) being twice the corresponding figure for the steam-hydrocarbon reforming process, which supplanted it in the sixties. Subsequent developments in coal gasification technology centred around the use of coal instead of coke, oxygen instead of air, use of powdered coal in suspended or fluid-bed reactors, and of higher pressures or higher temperatures of reaction. Plant designs changed with the introduction of centrifugal steam turbine drives leading to closer integration of process and motive steam systems on the total energy concept, limited, of course, by the unique nature of the feedstock which requires separation of large quantities of unreacted ash from the system at a fairly high grade of heat which is thereby lost. Nevertheless, design improvements both in gasification and in down-stream gas purification units, led to the achievement of a total energy consumption in the range of 11 to 12×10^6 K. cal/tonne of ammonia which is a distinct improvement.

Three processes are currently under commercial exploitation, viz. Koppers-Totzek, Lurgi and Winkler's processes.

Koppers-Totzek Process: In this process, finely pulverized coal is gasified in a co-current suspension with oxygen and steam at a flame temperature of about 2000°C and a gas exit reactor temperature of 1400 – 1500°C . Owing to the high temperature of reaction, which takes place at atmospheric pressure, all hydrocarbons in the coal are converted to carbon monoxide, carbon dioxide and hydrogen, the product gas containing only traces of methane and no other higher condensable hydrocarbons or tar. The bulk of the ash leaves the bottom of reactor in a molten state, and after granulation in a water bath is continuously removed from the system by a scraper conveyor. Fly ash is carried along with the raw gas through a waste heat boiler system comprising a radiation and a convection section, following which it is separated in cooling washers and 'special' disintegrators leaving a raw gas which passes to a gas holder. The dust content is further reduced in an electrostatic precipitator before the gas is pumped by crude gas compressors through the gas

purification units. These consist, in modern plants, usually of Rectisol hydrogen sulphide removal system followed by carbon monoxide shift conversion, Rectisol carbon dioxide removal, liquid nitrogen wash, compression and synthesis.

Lurgi Process: This process uses fixed bed reactors in which sized coal of 0.3–3.0 cm. size is gasified with steam and oxygen in a counter-current flow, at a pressure of about 30 atmospheres and a temperature of 750° to 850°C . At intervals fresh feedstock is charged into the top of the reactor and ash removed from the bottom through ingenious pressure lock systems. Because of the reaction conditions, the raw gas contains besides carbon monoxide, carbon dioxide, hydrogen, some 10 per cent by volume of methane, and condensable hydrocarbons, like benzol, light oil, naphtha, tar, phenols and ammonia liquor formed by the devolatilization of coal at relatively low temperatures. Separation of these condensates, their further processing, treatment and disposal, either as saleable product or effluent or both, are significant features of the Lurgi process.

Winkler Process: In this, small particles of coal or lignite are gasified with oxygen and steam in a fluidized bed at atmospheric pressure. The Neyveli plant in South India is based on this process.

Future Developments: A major element of cost in coal gasification is the air liquefaction and oxygen plant which can be appreciated from the fact that, depending on the process and the ash content of the coal, well over a tonne of oxygen can be required for gasification for every tonne of ammonia made. To eliminate this element of cost and to improve the overall efficiency, considerable development work is in hand, particularly in the USA, to evolve gasification processes in which heat of reaction would be supplied not by internal combustion but by an external medium, like dolomite (CO_2 acceptor process) or sodium carbonate (Molten salt process) or even by nuclear energy. It is likely that within the next few years, one or more of these processes would be established commercially for pipeline gas production, and it could then be a matter of time only before it is found successfully applicable in ammonia synthesis gas production. Reportedly, efforts are also in hand to modify some of the existing fuel oil partial oxidation processes for using coal, possibly in the slurry form.

Likelihood of technological obsolescence is, therefore, a matter of serious concern to prospective investors in coal-based ammonia plants.

Two Main Processes—A Comparison

Comparing the two main available processes, viz. Lurgi and Koppers-Totzek, the following broad observations can be made :

Coal Consumption : In spite of methane and other by-products (each mole of methane on subsequent reforming gives 4 moles of hydrogen) in the Lurgi gas, the hydrogen output per unit coal feed to gasifier is higher in this process than in Koppers-Totzek. Feedstock coal consumption in the Lurgi process could, therefore, be correspondingly lower. Against this of course one must take into account that Koppers uses ground run-of-mine coal whereas the Lurgi gasifier feed comes after sizing/grading process where some losses/rejects are possible.

Coal Quality : Koppers process appears to be relatively more flexible with regard to coal quality, particularly coking and ash fusion characteristics.

Oxygen Consumption : This is lower in the Lurgi process.

Energy Requirement : Primarily because of a larger air separation unit, low pressure and high temperature operation of the gasifiers, the energy requirement in a Koppers plant is higher than in a Lurgi plant of the same ammonia capacity.

By-Products/Effluents : The Lurgi process is somewhat more complex to operate owing to the need for separation, treatment and disposal at various stages of the process, of tars, mono- and poly-hydric phenols, light oil, benzol, naphtha, etc. The cost of these operations can only be offset if the by-products can be successfully marketed. In setting up a purely ammonia-based fertilizer plant one has to bear this in mind. The case is obviously different (as at Sasol in S. Africa) where a wide range of hydrocarbon fuels and chemicals are to be made from coal by gasification and subsequent Fischer-Tropsch reactions.

Maintenance Cost : There are two features of the Lurgi process which could lead to relatively higher maintenance costs : Problems of corrosion and fouling arising from the nature of the side products and mechanical problems in high pressure gasifiers with moving parts. This is, however, not to underestimate the problems of corrosion/erosion in equipment downstream of the gasifiers in the Koppers process through the presence of abrasive ash and dust particles.

Generally the maintenance cost of coal-based plants will be much higher than naphtha or fuel oil-based plants of the same capacity because of the nature of the

feedstock, effluents, mechanical handling equipment performing arduous duties and multiplicity of gasifiers.

Sensitivity of Process to Coal Quality

Coal, by reason of the conditions under which it is formed in nature, is a far more heterogeneous feedstock than any petroleum derivative. Analysis of coal can vary within wide limits even in samples drawn from the same seam within a localized area, as the following typical example illustrates.

Range		Range	
Moisture	7-10 %	Carbon	52-60 %
Ash	15-25 %	Hydrogen	3.4-3.8 %
Volatiles	28-32 %	Nitrogen	1.0-1.3 %
Fixed Carbon	40-46 %	Sulphur	1-2 %
Calorific Value (K. cals./kg.)	5200-5900	Hardgrove Index	57-67
Ash Softening temperature		1130-1230°C	
Hemispherical temperature		1360-1400°C +	
Flow temperature		1400°C	

The range in coal analysis would also depend on the method of mining and the extent to which dirt bands are included.

Variations in composition and physical characteristics of coal can have serious effects on the operating efficiencies in a coal-based process. It would not be out of place to review briefly the influence of some of the important coal characteristics on design and operation of coal gasification plants.

Reactivity : The reactivity of coal depends principally on its chemical composition and volatile matter, lignite and anthracite representing the high and the low extremes of the scale. In gasification processes a lowering in coal reactivity has to be countered by higher residence time (decrease in throughput for a reactor of a given volume), or greater fineness (Koppers), or higher temperature (affecting oxygen consumption) or a combination of these.

Carbon Content : Other things being constant, higher the carbon content of coal, higher the gasifier output.

Ash Characteristics : In Koppers process, gasifier temperature has to be maintained at a level higher than the ash melting temperature (hemispherical drop). Higher temperature implies higher production of carbon dioxide, which reduces gasification efficiency and hydrogen output. Apart from this, too high or too low an ash fusion temperature or too wide a bandspread might introduce complications by way of buildups inside the gasifier, slag formation in the 'neck' of the gasifier, rapid fouling of waste heat boilers, etc. In the Lurgi

process, where ash is removed as a solid from the base of the gasifier, a lowering in ash fusion temperature has to be countered by a lower temperature at the grate which in turn would affect the process efficiency. Generally, higher the ash content, lower the throughput of the gasifier.

Sulphur: Higher the sulphur content of coal, lower the hydrogen production, owing to formation of hydrogen sulphide.

Nitrogen: Nitrogen influences formation of ammonia and of hydrocyanic acid (by reaction of ammonia and carbon monoxide).

Other Impurities: Impurities, like magnesium, calcium, chlorine, etc., can adversely affect gasifier operation in a variety of ways.

Varying Feedstock to Process

In the technical literature issued by process licensors due cognizance is taken of the above variabilities of process and feedstock by quoting ranges, sometimes rather wide, in process conditions, efficiencies and, consumption figures. However, when it comes to actual design of plant, catering to a wider range in coal characteristics could only mean a more expensive and probably less efficient plant, optimization is, therefore, necessary and ideally the plant should be designed for a particular coal deposit, thoroughly defined with respect to stratigraphy, exploitable reserves, mining methods, extent of separation of dirt bands, maximum possible range of physical and chemical properties and last, but not the least, actual performance in pilot plant evaluation of a cross-sectional number of samples. The ramifications of this concept are as follows :

Captive Source of Coal: This is a *sine qua non* for a coal-based fertilizer plant. It means that throughout the life of the plant it will need to be assured of coal from a particular seam or seams, localized and mined specifically for the particular project. For a, 900 tpd ammonia plant with in-plant power generation total recoverable coal from a captive source should be of the order of 30-50 million tonnes. The fertilizer plant should be placed within 5 km. of the pithead with its own mechanical conveying facilities. Considering the complexities of a coal-based ammonia plant, the captive coal deposit should preferably be an open-cast facility with a favourable overburden ratio.

The location of the deposit can be decided only after extensive sampling, analysis and pilot plant evaluation. Other pre-requisites, like abundant water supply, effluent disposal facilities, availability of labour, proximity to

the market area, transportation facilities, etc., have to be satisfied. The preliminary expenditure on selecting a suitable location and evaluation of the deposits can, in view of the aforesaid, amount to a considerable sum.

Coal Washing: In order to improve the quality and the homogeneity of the feedstock, the economics of using washed coal should be given due consideration at the outset. The overall economics of such a scheme should be examined in the light of the following : (a) Possibilities of reducing capital costs if the coal mining, preparation and handling operations are integrated with a washery ; (b) operating economies which can be achieved by enriching the feedstock and improving its homogeneity ; and (c) in-plant thermal power generation and off plot steam generation from the 'middlings'.

Scale-up and Multi-Streaming of Gasification Plant

One of the first considerations in design of coal gasification plants is the capacity of the individual gasifier. On this will depend the extent of multiple-streaming required for a plant of given capacity. While the economics of scale fairly point towards single stream philosophy downstream of crude gas preparation, i.e. in hydrogen sulphide and carbon dioxide removal, CO shift conversion, nitrogen wash, synthesis loop, the air separation unit and the principal drives, there is at present insufficient operational experience to indicate the extent to which advantage could be taken of economy of scale in the gasification section.

The following table illustrates the point with reference to some of the Koppers-Totzek gasifiers.

Plant	Year of Commissioning	No. of Gasifiers	Total NH ₃ Capacity, tpd	Feedstock
Ptolemais (Greece)	1962	4	270*	Lignite
Kutahya (Turkey)	1968	3+1	340	Lignite
Modderfontein (S. Africa)	1974	6	1000	Coal
Talcher	1976	3	900	Coal
Ramagundam	1976	3	900	Coal
Korba	1977	3	900	Coal

*before extensions

Waste Heat Boilers: Beyond the gasifiers, the only significant area where scale-up problems could be significant in design are the waste heat boilers which face an arduous duty in view of the solids content and impurities in the gas. Here design changes with respect to geometrical arrangement and increased steam pressures need to be judged cautiously with an eye towards previous operating experiences.

Spare Gasifier Train: Both Lurgi and Koppers normally recommend a spare gasifier and waste heat boiler as installed standby. Not all plants, however, adopt this philosophy, possibly because gasifiers by themselves have a fair overload capacity (10-20 per cent). The question can probably be resolved only by careful analysis of the history of breakdowns in various sections of operating coal-based plants and subjecting the data to a Monte Carlo type simulation exercise.

Problems in Multiple-Streaming: Clearly, multiple-streaming in the gasification section is adopted in design for reasons of additional down time in this section needed for periodic cleaning and scheduled/breakdown maintenance. Multi-streaming can, however, have its own problems, for example, (i) operability problems connected with a number of gasifiers and waste heat boilers generating high pressure steam in parallel, when individual gasifiers are shut-down for their frequent, if short, maintenance outages, e.g. shut-down, isolation, recommissioning, etc., (ii) for identically designed multiple units, mechanical failure in any one unit is more often than not repeated in the other units, with the result that total loss of plant availability as a result of such unscheduled breakdowns is no different for a multiple unit than for a single-stream plant; and (iii) there might be problems in plant balancing at turned down rates of operation not only with respect to parallel operation of the multi-streams at divergent rates but also constraints imposed by minimum turn downs possible in the single-stream sections of the plant, e.g. turbine drives.

Operational Problems

The present authors had the opportunity of visiting some of the operating coal-based plants in Europe. Unfortunately, the plants are relatively small in capacity, sometimes built over a number of phases, and incorporating electric motors and reciprocating compressor drives. As such, they do not afford a direct comparison with the larger capacity total, energy units now being conceived. Feedstock composition and analyses are again not strictly comparable. From general observations made of the operation of these plants, however, the following potential problem areas should receive adequate attention in the design of future plants, with a view to achieving a high capacity utilization factor.

(i) *Location:* The lignite in one of the plants visited is obtained from a nearby open-cast mine and conveyed in hopper type rail trucks. The dry ash from the plant is transported back for filling the stripped areas of the

mine, thus providing a solution to the problem of ash disposal and the ecological requirements of the mined area. The desirability of returning the ash to the mined area should be considered in new plants located at pithead.

(ii) *Feedstock Handling & Preparation:* This undoubtedly is the unpleasant feature of all coal gasification processes when compared with the neat and tidy petroleum feedstock-based ammonia plants. The basic operations are, however, no different from thermal power plants. Smouldering spots on coal heaps are unavoidable in large coal yards, e.g. in thermal power plants, but in an ammonia plant design some thought should be given in maintaining appropriate distances from the hazardous areas and in locating the coal yard and the coal preparation units in relation to the overall layout of the process units. Likewise, the coal dust, which could find its way into the gas purification systems as also the cooling water recirculation systems should be safeguarded against. Given adequate consideration at the design stage and with judicious mechanization, there is no reason why a coal handling and preparation area cannot be amenable to good house-keeping.

(iii) *Problems With Fly Ash & Slag Formation:* One must consider in great detail and pay utmost attention to the question of removal of the entrained fly ash in the raw gas, otherwise corrosion, erosion and fouling of downstream equipment could take place. In this connection, use of electrostatic precipitators between the gas-holder and the raw gas compressors, in Koppers-type of plant, should be incorporated to safeguard the compressors.

As mentioned earlier, the fusion temperature characteristics of the gasifier residues should have sufficient margin to prevent slag accumulation at the gasifier outlets.

To prevent prolonged shutdowns for repairs and cleaning of deposits adequate consideration should be given in providing suitable devices and/or access for quick cleaning.

Coal sludge and ash settling areas could create problems. Steps should be taken to minimize the dust content of any recycle of 'settled' water otherwise choking of the sprays in the cooling washers could take place. A purge and lagoon system is needed to deal with the settled sludge. Open channels carrying ash from the plant could get fouled up with hard deposits due to silica and lime in the ash.

(iv) *Erosion/Corrosion*: Hydrogen sulphide corrosion of ash removal chains and conveyors should be guarded against. Likewise, erosion of pipes conveying powdered feedstock could create problems.

(v) *Other Design Features*: By now the various trip systems and safeguards associated with plants dealing with liquid hydrocarbon feedstocks and oxygen are well recognized. In a coal-based plant more attention is perhaps warranted because of the solid nature of the feedstock to ensure satisfactory isolation and sensitivity of the trip systems.

The problems which could arise due to the presence of coal dust cannot be over-emphasized. Considerable thought and ingenuity will be required in siting and protecting plant, machinery and instruments. The standards normally adopted for thermal power plants against the nuisance of coal dust will not be adequate for large single stream ammonia and urea plants sited adjacent to a coal gasification unit.

(vi) *Problems with By-Products*: As mentioned earlier, in the low temperature gasification process, the by-products could give rise to problems. Fouling with tar could interfere with level control elements besides affecting heat transfer in waste heat boilers. There could also be problems with hydrogen sulphide and hydrocyanic acid formation in the process. Separation of by-products in this process is, however, a separate and arduous discipline on its own rights which has to be taken very seriously to ensure smooth operation of the plant. The disposal of the aqueous effluent from the plant will also require special attention.

Application of Total Energy Concept

Operational complexities, as can be judged from the foregoing, are of a higher order in an ammonia plant based on coal than on petroleum feedstocks. The question could, therefore, rightly be asked as to whether it would be prudent to further increase the complexity of operation by introducing a large number of steam turbine drives, which would call for complicated control and trip systems liable to malfunction, several levels of steam pressure in the plant and generation of steam in gasifier waste heat boilers at as high a pressure level as possible notwithstanding lack of previous experience. The question becomes more plausible if one considers that for a pit-head plant, additional availability gained through installation of a less ambitious but more proven system, plus the economy of scale derived from a larger power station could swing the balance in favour of a greater use of electrical drives, in spite of reduced overall energy efficiency. Possible use of gas turbines

for power generation introduces yet another approach that could perhaps be integrated more closely with the coal-based process than current schemes which seem to concentrate almost solely on pressure of steam generation in the gasifier boiler as the index of application of the total energy concept.

Another very useful investigation towards improvement of overall energy efficiency of the process would be (in the Koppers process), to find a method of heat recovery from the 300-350°C raw gas after the waste heat boiler and before gas washing. To what extent this could be done by adopting raw gas shift conversion (using Cr-Mo oxide catalyst) before sulphur removal is perhaps worth exploring.

Conclusions

1. Sinking vast funds in rupees and in scarce foreign exchange on a number of coal-based fertilizer plants would be for India a most serious consideration which in spite of the urgency of the situation, must be approached with the utmost caution.
2. Detailed examination of plant records from operating coal-based plants should precede choice of process and design optimization.
3. Exhaustive preliminary work would be required or evaluation of specific coal deposits which, if found suitable for the selected process, should be earmarked as captive sources for coal-based plants. In this connection a vigorous extension of the work already done at CFRI is indicated.
4. The key emphasis should be on plant availability, since by the time the next generation of coal-based plants reaches maturity, say, in the early eighties, technological obsolescence might have already set in.
5. Design criteria used, particularly in departures from past and proven design, must be examined very carefully before process/equipment selection.
6. Extent of application of the total energy concept through steam turbine drives and HP steam generation in process waste heat boilers should be examined critically with an eye towards the effect on plant availability, downtime and maintenance costs.
7. Optimization through integration of coal washery, coal gasification and power generation should be seriously considered.
8. A concerted effort should be made towards bringing forward the completion date of at least one of the three coal-based plants now under construction in India, with a view to utilizing its operational experience in the design of the next generation of plants.

Fundamental Concepts in Determining the Choice of a Technology Policy for the Developing Countries with a Low per capita Resource Base*

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This paper deals with factors relating to a policy for technology transfer from advanced countries to the developing countries with a low per capita resource base. Employment creation is a core problem for all such countries which will remain so for several decades. This is in sharp contrast to the problems of the developed countries where generally there is an inadequate supply of labour force to sustain the development efforts. There is one other striking dis-similarity ; there is an abundance of goods available in the developed countries with sound economic infrastructure facilities and the problem is to find market for them ; in the developing countries, however, the demand outpaces supply almost in every commodity and infrastructure facilities are inadequate.

A technology policy for a developing country would have to carefully recognize these basic differences in national development needs and thereafter proceed to identify the types of technology that would be suitable for transfer. Generally speaking, the types of technologies which would help to counteract the weakening per capita resource base in the developing countries would be a logical choice. They would include more effective utilization of land resources—both for agriculture and exploitation of minerals—exploitation of marine and energy resources and replacement of scarce mineral resources with newer synthetic materials.

The basic requisites of technology transfer have been outlined. The status of technology, the techniques of evaluation, the mechanism of transfer and the role of international agencies in promoting such transfer are some of the aspects which have been broadly covered. The status of technology has been identified into 3 categories depending generally on the state of readiness of the technology for commercial use, viz. (i) buy and use directly, (ii) buy and adapt for local conditions and thereafter use, and (iii) buy, develop further and use. A judicious blend in the transfer of technologies from all these categories are required to attain a rapid rate of economic growth and in self-reliance.

The third category is indeed of importance to widen the base of scientific talent and development of R & D infrastructure facilities in the developing economies. They could not, however, be subjected to the rigorous cost-benefit analysis but it would be worthwhile to take calculated risks in choosing such of them which would yield potential national benefit.

A technique for evaluation of technologies which are in different stages of readiness has been outlined in this paper and a semi-quantitative approach suggested. It involves analysis after assigning arbitrary values of net return (R), further costs and forecasts of estimates (C), probability that research will be successful (P) and the probability ratio of success (PR). Judicious values to these variables could be given by experienced technologists, engineers and economists and a broad judgement arrived at in evaluating the status of technology by use of a formula, viz. $PR = P \frac{R}{C}$. This formula, however, would yield a good correlation only in case of technologies which are in a state of near readiness.

It follows that the evaluation of technology and decisions leading to purchase of know-how should necessarily have to be taken by knowledgeable scientists and engineers who are directly involved in identical or similar fields of activities. It is not adequate to consider that every technocrat is capable in evaluating these highly complex factors.

The mechanism of transfer, such as direct purchase through licence agreements for commercial exploitation (or as components of turn-key contracts) would only be applicable to those which have already been proved in commercial establishments and on which evaluation of performance of commercial undertakings actually built elsewhere are possible. In such cases, it would be desirable to avoid formation of multinational corporations.

The same consideration would apply, more or less, for those technologies which are in a state of readiness for commercial exploitations but which require further limited development work of adaptive type to suit local conditions.

* Read at the International Seminar on Technology Transfer held at New Delhi under the joint auspices of UNIDO and CSIR, Govt. of India, during December 11-13, 1972.

Technologies, where the state of readiness is such that it shows potential and promise but would require further development work, could be sub-divided into two categories. First, which have been developed to a successful stage but not already exploited in commercial scale establishments. The areas of uncertainties are non-existent or are limited to clearly identifiable sections where experience from similar industries would result in commercial success. There would still be an element of risk involved in taking investment decisions with such technologies. In such cases, the technology transfer might be considered through the formation of multinational corporations. This would inspire confidence and reduce the risks with the direct involvement of those who have developed the technology.

The second category would be those technologies which have promise and potential but on which further considerable R & D efforts are required. It would be useful to obtain such technologies through formation of multinational corporations initially even for the development efforts through a pilot plant/semi-commercial plant scale. Such agreements should provide for suitable safeguards for sharing the benefits of development.

The role of international agencies in the transfer of technology has been indicated. Specialized agencies of the United Nations, for example UNDP/UNIDO, might consider to organize specific divisions in their activities exclusively (i) to promote technology transfer from the developed to the developing nations and bringing together countries on Government to Government basis. Such agreements should provide for implementation by the agencies nominated by the Government; and (ii) to organize international forums for innovation exclusively to create a meeting-place for the trading of licences, know-how and advanced technology. Such arrangements would offer unique opportunity to get a visual understanding of the potential implied in a licence offer, the background and status of the licence of the company as well as the licensed object in question.

Philosophy & Basic Constraints in Determining National Technology Policy

This paper deals with factors relating to a policy for technology transfer from advanced countries to developing countries with low per capita resource base. It excludes developed countries, e.g. Japan, which is developed but has a low per capita physical resource base; it also excludes developing countries in the Arabian Gulf which are under-developed but generally have a high per capita financial resource base.

The problem of employment creation will be the core of all issues for the developing/underdeveloped countries for next two to three decades. Recent U.N. projections indicate that the labour force between ages 15 and 64 in the countries of Asia and the Far East is expected to increase by nearly 700 million or 61 per cent by 1990. The number of new persons needing jobs is growing faster in many cases than the actual population. The high birth rate of the past decades produced the Asian working population of more than a million last year i.e. 55 per cent of the total. The population in the region by the end of the century is likely to exceed 3,500 millions i.e. 4 times of the present total; family planning targets that have been taken up, if implemented and its results are achieved completely, could reduce this by an estimated 164 millions only.

The problems of population increase, unemployment and low per capita resource base are going to remain as the basic core of all problems—social, political and

economic. Meaningful development efforts must necessarily take full cognition of these fundamental issues. In the development efforts, political and economic directions have to be necessarily given keeping the dimensions of the problems in perspective on the basis of such population projections. Technologies that would contribute towards reducing this problem should, therefore, be the logical and prior choice for all development efforts.

Developing/underdeveloped countries are often making the mistake of allowing demands of products which use scarce resources to grow recklessly causing distortion in the economy. To illustrate, the use of motor spirit for individually owned cars and kerosene for cooking has been allowed to grow for the benefit of a few millions of people in India and no efforts have been made to discipline such demands in order that the scarce resource of crude oil could be put to more meaningful use for the good of the economy as a whole. A fundamental point of importance for all developing/developed countries is thus to carefully scrutinize the demands and to set targets to discipline such demands first and identify such technologies for processing of resources which would fit into such national demand patterns.

Our world is indeed very unevenly balanced. Whereas, the developing/underdeveloped countries would look towards technologies to solve their basic needs, the developed countries of the West have indeed been facing

the problem just in reverse. Thus, the development in Western Europe and Japan has proceeded so fast during last two decades, in particular, that there has been a problem of an inadequate supply of labour force to sustain the development efforts. R & D efforts have emphasized on technologies suited to such needs and great stress is laid—probably rightly so—by the developed nations and R & D efforts are directed on extensive labour-saving, capital intensive devices to increase the growth rate of development to continually give a rising standard of living to the people of the developed nations.

There is one other striking dissimilarity between the two groups of nations; in the developed countries, there is an abundance of goods and the problem is to find a market for them; in the developing/underdeveloped countries, demand outpaces supplies almost in every commodity inclusive of often in basic commodities of food, clothings, building materials, etc. Here again, the developed countries have tended to emphasize on R & D efforts to changing technologies to adapt to their own changing economic needs.

In most of the developed countries where free enterprise is the general rule, commercial interests have played a significant role in the development of newer technologies. Such commercial interests lead to adoption of R & D efforts to changing commercial needs inclusive of development of labour-saving devices to meet the continual shortage in the supply of labour and rising costs in per capita labour input. Such technologies in most cases might not be of interest to the needs of the developing nations, but very often developing/underdeveloped countries fall a prey to the glamour of new technology and the aggressive salesmanship in licence/know-how from the developed countries. Indeed, it is of fundamental importance for the national planners to recognize the crucial difference in the development needs of the two groups of countries. Technology transfer assumes a key factor in the complex processes of such decision making for national development efforts.

There need be no misunderstanding on the objectives that require be set clearly for this purpose. Whereas the problem of employment creation would continue to remain the core, it would indeed be suicidal to adopt technologies solely on their capacity to employ more men but are otherwise out-dated and obsolete. Developing countries have been very frequently making this mistake. Instead of strengthening, it would weaken the economy as industries with lower productivity and

inefficient use of scarce resources would create high cost goods with disastrous consequence on the economy as a whole. The employment so created could only be at the cost of society, for such employees would live as parasites on the society without contributing meaningfully to national wealth.

This concept would appear to be apparently in conflict but indeed it is not so. Although on one side, the developing/underdeveloped countries would have to lay emphasis on creation of employment but at the same time, the obsolete technology needs to be discarded and newer technologies adopted which would contribute towards strengthening the economy as a whole in creating industries which could take full advantage of the development elsewhere towards more efficient utilization of resources to yield low cost products. Specifically, introduction of such technologies which would contribute towards a favourable balance of payments position and lessening of overseas dependence on strategic raw materials but not necessarily employment-oriented would be of importance. The choice of technology transfer thus becomes all the more complex and identification of technologies which would achieve the twin purpose should be the primary goal.

The philosophy of technology transfer must, therefore, be necessarily derived by a broader interest in the economy inclusive of social and political factors in advancing the development as a whole. Further, technologies involving national efforts to mobilize forces of science to bring about an earlier and fuller utilization of resources—resources in man, land, minerals, marine and on harnessing the nature, the atom and the sun as sources of energy—contribute towards enlarging the per capita resource base which, in turn, would lead to creation of additional employment in very large numbers.

Types of Technology and Areas of Development

The identification of the technology suited to the needs of the developing country must, therefore, be restrictive both as regards the type, manner of transfer and status, i.e. the state of readiness of such technologies at the time of transfer. The national R & D infra structure facilities and the need to be progressively 'self-reliant' in every facet of development efforts are other important factors.

The technologies which contribute to counteract the weakening per capita resource base of the developing/under-developed nations would be one logical

choice. There are many areas where such technologies could be fruitfully adopted. For example, often the availability of agricultural land is limited and the yield of product per acre therefore assumes great importance. Technologies in land use, water management, the identification in soil deficiencies, physiology of crop nutrition, the effect of climatic factors and factors contributing to the basic process of photosynthesis, means for protecting the crops from pests and diseases, etc. need be identified and carefully evaluated and adopted to suit the local needs.

The fixation of nitrogen by suitable crop rotation and/or by inoculation of suitable microorganisms is another area of importance. Technologies involving more efficient use of chemical fertilizers would go a long way to extend the widening gap in the availability of primary fertilizer nutrients. Further, development of newer types of fertilizers, or newer development in the application of conventional fertilizers, e.g. direct application of anhydrous ammonia, are areas of great economic significance. Technologies involving utilization of waste land would be another area in this category. It is important to note that agricultural technology which has proved useful in one country is not transferable as such to another country. The basic principles of science that have led to successful application of such technologies abroad are therefore to be evaluated and further development work undertaken to fit in with the local needs.

Newer technologies for effective and rapid prospecting of mineral resources, such as the newer techniques of oil prospecting both on shore and offshore, ground water survey and newer methods of rapid surveys on mineral resources, ought to receive higher priority.

The technology of using low grade minerals indigenously available, as for example use of low grade coal, phosphate rock, pyrites, needs to be identified for possible application. Often, economy tends to exploit the highest quality or the lowest cost resources. This has been particularly true in the exploitation of mineral resources. Once these are exhausted, one has to look towards lower grade materials. National development efforts ought to give priorities for exploitation of such resources in a rational manner.

Technologies to exploit the marine resources to extend the per capita resource base are becoming increasingly important. Mineral resources of the ocean could effectively bridge the food gap and more parti-

cularly the protein gap of the developing/underdeveloped nations. This is a relatively new field. A review of development in this field elsewhere and transfer of technology for possible use would indeed be an important area.

There is a rapid depletion world over of the popular source of energy, viz. crude petroleum. The oil resources of USA which at one time—only two decades ago—were considered high have already been depleted; the world resources elsewhere are also depleting fast to meet the increasing needs of the developed nations. Studies show (unless there are some very large discoveries to tilt this balance in the world supply position) that world resources of crude oil including those of tar sands (oil shales) and the Alaskan deposits could only last until about the end of the present century.

An increasing attention is now being given to harnessing the *Energy Resource* from other sources, viz. the sun, the atom and other fossil fuels. The developing nations would do well to consider transfer of technology in these areas and utilize them to fit in with the needs.

For India, the utilization of coal resources assumes added significance. The technology for processing the crude oil to obtain greater yield of products useful to the economy per unit of crude input need to be obtained from the developed countries to fit in with the needs of India. At the same time, technologies in the field of coal processing are to be obtained from other countries and further developed to replace the traditional petroleum source of raw materials for such important process industries, such as chemical, fertilizers, domestic fuel, etc.

The replacement of scarce mineral resources for conventional use are of particular significance for India. Newer technologies have been developed abroad to replace non-ferrous metals in many of the uses to which they are normally put in India, such as brass, aluminium, alloy steels with synthetic plastics. India even now uses a large tonnage of metals for dinnerware and household utensils. Much of these could be replaced by suitable synthetic plastics.

70-80 per cent and even more of the sulphur and/or sulphur bearing materials are being used in the developed countries for production of chemical fertilizers. Our sulphur resources are non-existent and that of pyrites are at best limited. There are process technologies which could eliminate or reduce the use of sulphur in

production of suitable chemical fertilizers. These are appropriate for Indian conditions.

Technologies for production of synthetics to replace cotton and wool to extend the per capita base of our land and animal resources would also be appropriate in this context.

The foregoing paragraphs would illustrate the areas for which suitable types of technologies need to be identified to fit in with the national priorities. Suitable technologies are available at different stages of development in the developed countries in many of these areas and their identification and transfer are of importance to the developing countries.

Patents & Inventions, Etc.

Solid State Annunciator*

In any modern industrial plants, such as fertilizers, chemicals, etc., it is necessary to maintain several parameters of the process, like the temperature, pressure, flow, level, etc., at some predetermined values. If, at any time, these parameters cross the set points in any stage of the process corrective steps must be taken to bring back the process into normal working condition. To accomplish this object the very widely accepted practice to provide audio-visual alarm systems either in the central control room for remote indication or on the field panel itself for local indication. The equipment commonly used for this purpose is the annunciators wherein the visual alarm and the audible alarm indications are achieved by employing electromagnetic relays in the instruments which can detect the faults developed in the plants. The relay contacts are, how-

ever, susceptible to dust, vibration and mechanical failures and therefore found to malfunction and give rise either to spurious alarms or missing wanted alarms. The industrial electric hooter used in this conjunction suffers from the drawback that it can not be kept accidentally energized for longer lengths of time without endangering its life.

The solid state annunciator has therefore, been developed to take care of the aforesaid defects. This system employs completely transistorized circuits and eliminates the usage of all moving contacts, such as those associated with the relays. An electronic power amplifier with an integral audio oscillator acts as an electronic hooter and replaces the conventional electric hooter.

In addition to the advantages mentioned above the solid state annunciator has

several other inherent advantages compared to the relay type versions. They are : (1) Capability to tolerate long load-length resistance extending up to a few Kilo-ohms, (2) Very low power consumption, (3) Intrinsically safe circuits, (4) Very small space requirement, (5) Light Weight and long life, (6) Ease of maintenance through adaption of throw-away plug-in circuit cards and (7) Availability of a variety of pitch of the tones for the electronic hooter, etc. This system employs 100% indigenous components. Its complete know-how is sold to M/s. Instrumentation Ltd., Kota for commercial exploitation.

*Patented under Indian Patent No. 133002 (Inventors: K. G. Krishnayya and J. Satyanesan, P. & D. Division, F. C. I. Ltd., Sindri)

A Conferences & Seminars

Coal as Feedstock for Fertilizer Production

A symposium on coal as feedstock for fertilizer production was held under the auspices of the Fertilizer Association of India at New Delhi during April 29-30, 1974, under presidentship of Sri Shah Nawaz Khan, Minister of State in the Ministry of Petroleum and Chemicals. In welcoming the delegates, Dr. S. K. Mukherjee, Chairman FAI and Director (Production), Fertilizer Corporation of India Ltd., stated that India's plans would place her among the first three or four largest producers of nitrogenous fertilizers in the world. Today, the industry's capacity is around 1.94 mil. tonnes of nitrogen and in ten years from now (1985-86), the perspective plans call for an increase to nearly 10 mil. tes. The projects that are in production or under construction, amount to a total capacity of a little over 4 mil. tes, of which about 2.2 mil. are based on naphtha requiring more than 2.5 mil. tes of naphtha. The projects under construction, approved for construction for the next 5 years and under contemplation call for nearly 2.9 mil. tes of nitrogen production requiring more than 3 mil. tes of fuel oil/heavy residues from petroleum sources. Since the industry at present has been planned to use nearly 1 mil. tes of petroleum fuel oil for raising steam, the planning of the industry would call for nearly 7 mil. tes of petroleum products, i.e. naphtha/fuel oil/heavy residues.

Out of 4 mil. tes of that was estimated for production at the end of 1978-79, only about 684,000 tes or about 17% of the total is based on coal. Because the price on crude petroleum involving a large outflow of foreign exchange, there is no alternative but to shift from oil to coal. The present production (100-110 mil. tes) of foodgrains shall have to be stepped upto 170-200 mil. tes in course of the next 10 years to give stability to our economy. Plans for judicious recycle of organic wastes to improve our soil would turn such wastes into assets, but increased use of chemical fertilizers is inescapable to increase the per acre yield of our limited agricultural land.

Continuing, Dr. Mukherjee stated that we have adequate resources of coal but

we would require time to develop coal resources and gear up the transport system to move coal to consumption centres. So despite our critical balance of payments we might have to depend for a short-term on petroleum feedstocks for fertilizer production. Our plan should, therefore, remain flexible to ensure that in the medium term we have to change from petroleum-based feedstocks to coal and our immediate planning for major fuel-based projects had, therefore, to take that aspect into account.

Sri Shah Nawaz Khan, in his presidential address, laid stress on the use of non-coking coals as feedstock for nitrogenous industry. The total nitrogen capacity planned including capacities in operation, under construction and approved for implementation would require annually about 25 lakh tonnes of naphtha, 30 lakh tonnes of heavy petroleum fraction and 8.6 lakh tonnes fuel oil as energy source. The equivalent tonnage of petroleum crude would involve an import bill of over \$ 450 million. Stressing the need for concentrated effort to reduce consumption of petroleum feedstocks, he stated that in some plants consumption of naphtha was higher than the design norms to steps would be taken to save naphtha. However, it would be necessary to examine the implications of a change-over to coal of plants in which fuel oil was used for steam generation as they were located away from coal mines. He commended the application of organic wastes to the soil after suitable processing. Concluding, Sri Shah Nawaz Khan said that suitable pricing policies and fiscal measures would have to be developed so that fertilizer manufacture from coal, which requires heavier capital, was commercially viable.

Inaugurating the symposium, Sri K. D. Malaviya, Minister of Steel and Mines, made a strong plea for the utilization of all organic wastes in conjunction with chemical fertilizers and also of our water resources and inorganic wastes. Dealing with coal as an alternative feedstock, Sri Malaviya said that it presented many technological and economic problems but we have to face them if we want to use our indigenous sources.

Session I : In the first session, which was chaired by Sri K. S. R. Chari, Secretary, Union Ministry of Steel and Mines, New Delhi, 2 papers were presented. In his introductory remarks Sri K. S. Chari admired the courage and foresight of FCI Ltd. and the Ministry of Petroleum and Chemicals for taking the decision in 1969 for putting up 3 coal-based fertilizer plants knowing fully well the improper functioning of the then coal-based plants, viz. at Sindri, Neyveli and Rourkela. While the total coal resources were estimated at 80,000 mil. tes, non-coking coals accounted for 60 thousand mil tes. The location of a coal-based plant primarily had to be near the pit-head. Then the transport of washed coal by pipeline or converting coal at the pit-head into gas and then transporting this gas over 200 to 300 km would have to be examined. The experience at Neyveli was not encouraging and this needed further study whether a different technology or process was to be adopted for lignite.

Out of 83,000 mil. tonnes of coal and lignite reserves in India, nearly 75 per cent is non-coking coal substantially suitable for fertilizer manufacture. By the end of the Fifth plan the production of coal is to increase from 78 to 135 mil. tonnes, which by the end of the Sixth plan may be over 200 mil. tonnes. The major workable coal resources belong to the Lower Gondwana series occurring in W. Bengal, Bihar, M.P., U.P., Orissa, A.P. and Maharashtra. Besides these, there are tertiary coals in Assam and Jammu and lignite deposits in Tamilnadu, Rajasthan and Kutch. Keeping in view of the large resources of non-coking coals, the authors of the first paper¹ have identified the coals of different areas coalfieldwise suitable for use as feedstock for the manufacture of nitrogenous fertilizers (Fig. 1).

The Rajmahal coalfields in eastern Bihar have an estimated reserves of about 2700 mil. tes comprising high moisture, high volatile non-caking coal, but require detailed proving for establishing their quality. However, investigations carried out by GSI in parts of the coalfield appear to indicate that there are seams of varying thickness from 1.2 to 8 metres which may contain coals suitable for gasification.

There is a possibility of establishing a half-a-million tonne urea plant by the end of 6th or early 7th Plan. The present difficulty is that there is no infrastructure available in the area with railway line 64 km. away.

Large resources¹ of high moisture, high volatile good quality non-caking coals in a virgin tract known as Jhanjra in the East Raniganj coalfield, about 21 km. from Durgapur and well connected by roads and railway, have 9 seams proved, of which 5 older seams contain better quality coal. The estimated gross reserves are 590 million tes and it should, therefore, be possible to have a half-a-million tes urea plant in the sixth plan period, unless this coal is not eventually linked up with such priority projects, like a coal-to-oil unit and other industries. In fact, it is possible to increase the capacity to 1 mil. te if the good quality Jambad-Bowlah coal from the other parts of Raniganj coalfield is made available.

A virgin tract, known as Chapri block (20 sq. km.), in the north-eastern part of the East Bokaro coalfield, has a good quality seam (reserves 65 mil. tes). The coals are low moisture, low volatile caking type and can be utilized for fertilizer manufacture, if not utilized in coking blends. Subject to further investigations this coal can be utilized for a half-a-million urea plant in the Sixth plan.

The S. Karanpura coalfield is having a total reserves of over 2000 mil. tonnes in its 42 seams; the Argada and Sirka seams of the Gidi, Bhurkunda and Sirka collieries (total about 240 mil. tes) are sufficient for a half-a-million te urea plant. Besides, there are seams, like Kurse, Up. Nakari, Lr. Nakari, Up. Semana, Lr. Semana and Hathidhari, which have good quality coals. In the North Karanpura coalfield, the coals from Bachra group of seams are thin and about 100 mil. tes are available and it may be possible to set up a half-a-million tonnes fertilizer plant in the 6th Plan, if adequate quantities of good quality coal can be raised and some of the present consumers delinked.

Of the 5 seams in the Hutar coalfield (Palamau Dt., Bihar), only 3 are workable; large tracts are lying virgin. According to the authors, a half-a-million te coal-based

Coal Resources for Nitrogenous Fertilizer Plants by S. K. Bose, T. N. Basu and D. Basu, Deptt. of Mines, Ministry of Steel and Mines, New Delhi and Coal Mines Authority Ltd., Ranchi.

urea plant can possibly be located in this area during the 7th plan, subject to the proving of the reserves which might be significant. This area has locational advantages for movement of fertilizers to northern India.

In M.P.'s Bistrampur coalfield, the coals of Bhatgaon block and Khargaon and Sonagara areas having reserves around 100 million tonnes are quite suitable for fertilizer manufacture and therefore it is possible to set up a half-a-million urea plant in this area during the Sixth plan. The coal blocks are 6 to 12 miles away from railway line. In the *It* river coalfield, there are 2 seams which are of appropriate quality but large virgin tracts exist which if found suitable can be sufficient for setting up a half-a-million te urea plant in the 7th plan. No regional investigation has yet been carried out to prove the existence and disposition of the seams at depth as well as the occurrence in other parts of the field. In the Kamptee area (Maharashtra), large resources (100 mil. tes) of coals suitable for fertilizer manufacture exist; there was a proposal to set up a fertilizer factory in this region as a joint venture between Maharashtra Government and the erstwhile owners of the Kamptee colliery. In the Chanda area, there is a thick seam (20-25 m.), whose bottom (4-5m.) section is likely to be suitable for manufacture of fertilizers, say in the 7th plan.

There is a virgin coalfield south of Bistrampur coalfield, known as Lakhanpur coalfield, in which 2 seams (Nos. 1 and II) are comparatively better having total reserves of about 100 million tonnes, for which detailed geological investigations are required to establish the same more precisely. As there is no infrastructure in this area at present, a fertilizer plant can be contemplated only towards the end of 7th plan. However, mainly seam I is extractable.

The Singrauli coalfield located in U.P. and extending upto M.P. has primarily two seams, known as Turra and Purewa. It has huge reserves and so has strategic importance of supplying coals to the northern India for fertilizer manufacture after deshaling and washing. Good sources of such coals occur in Turra seams. It may therefore be possible eventually to set up fertilizer plants not only in the Singrauli coalfields itself but also at locations in northern India for supplies of such washed coals for meeting the regi-

onal demand. Programming would, however, depend upon the capacity to produce additional coals from thick Turra seam alone from the Singrauli coalfield, possibly in the 6th or in the earlier part of the 7th Plan period. Large scale washability tests and utilization coordination for each product will be needed.

In the second paper², read by M. M. Sen (CFRI), the authors gave general quality specifications of coal for established gasification processes for the manufacture of synthesis gas. For fixed bed atmospheric air gasification, coal of close size is essential for achieving higher efficiency and fines below 8 mm. should be kept at minimum. In Lurgi process coal of size 3 mm. and above is used and the ratio of diameters of the largest and the smallest particles in the feed should not exceed 5 and a maximum of 10% fines below 3 mm. is tolerable and thus a less friable coal is preferred. In the Winkler's process coals of —10 mm. size are used while in Koppers-Totzek the feed size is over 80% through 200 mesh, so a coal having good grindability index is desirable; unfortunately most of the Indian non-caking coal are poorly grindable (H.G. Index 40-60).

The upper limit of ash in Lurgi process is 30% with the ash fusion characteristics an important factor, in Winkler high ash adversely affects the reactivity of the coal, while in Koppers coal upto 35% ash can be tolerated. However, with higher ash both fuel and power consumption will increase per volume of synthesis gas production. Suspension-type gasifier can be operated under slagging conditions. The upper limit for moisture in fluidized and entrained-bed (Winkler, Koppers) is about 10% while in fixed bed (Lurgi) upto 30% moisture can be tolerated.

The total coal resources are about 81,000 mil. tes occurring in about 9 States. The production of coal is largely confined to Gondwana formations in the Peninsular area south of Ganges. The coals of Peninsular India are usually low in sulphur (less than 0.8%). The non-caking coals available in A.P., Bihar, M.P., U.P., Maharashtra and W. Bengal are suitable for synthesis gas manufacture.

2. Indian Coals and Their Suitability for Production of Nitrogenous Fertilizers by A. K. Moitra, N. C. Sinha and K. C. Lahiri, Central Fuel Research Institute, Dhanbad.

Session 2: Sri K. C. Sharma, Chairman and Managing Director of F.C.I. Ltd., who chaired this session, described in his opening remarks the history of the installation of coal-based fertilizer plants in India. FCI Ltd. had visualized in 1962 that coal-based plants should also be installed but the Government later revised its decision and the project at Korba (M.P.) had to be abandoned after spending over \$ 1 crore. Dr. K. R. Chakravorty, the then Technical Director of FCI, persisted in his views and ultimately succeeded in obtaining approval for 3 large coal-based plants. Accordingly to Sri. Sharma, Dr. Chakravorty is the father of coal-based fertilizer plants in India. If this approval for the installation of the first coal-based plant planned in 1962 had not been withdrawn, the country would have ample experience of running coal-based plants by now and many more plants would have been initiated. He was confident that there would be no difficulty in processing Indian coals as the process licensors of the two main processes, viz. Koppers and Lurgi, have analysed Indian coals extensively and found them suitable.

Dr. G. Hochgesand presented P. Rudolph's paper³ in which the author mentioned that foreseeing energy shortage

3 The Lurgi Pressure Gasification and its Application for Ammonia Manufacture by Paul Rudolph, Lurgi Minero-Lothchink Gm 6 H, Frankfurt—on Main, W. Germany.

four years ago 5 U.S. gas companies in 1970 decided to build synthesis gas plants from coal, all based on Lurgi process and each to produce 250 MM scf/d high Btu gas. Nearly all grades of coal including high swelling and strongly caking coals can be gasified and most of the Indian coals being highly reactive are also very well suited. In addition, Lurgi has developed processes for low pressure methanol synthesis and oil by Fischer—Tropsch synthesis from coal.

It is generally accepted that gasification of coal should be carried out under pressure and that counter-current principle offers the best conditions for the efficient performance of the gasification reactions with the result that methane, tar, naphtha and ammonia are coproduced. The tests carried out in the Lurgi plant at Westfield (U.K.) under the sponsorship of the American Gas Association have shown that high swelling strongly caking coals are suitable for gasification and the range of coal which can be processed is very wide.

In the process, the r. o. m. coal is crushed and screened and 64% of the total coal is fed to the gasifier, while 36% is needed in the boiler for generating steam for the drives and for the process. For an 1000 metric tons ammonia per day unit, the gasification plant consists of 4 gasifiers, which helps in having a very high (91%) availability factor (Fig. 2). Moreover, the oxygen consumption is very low, which has a decisive influence

on the reduction of production cost. The active portion of the gasification agent is the steam because the hydrogen in the synthesis gas has to be manufactured mostly from a steam reacting with carbon in the gasifier and only a small portion is produced in the down-stream CO-shift conversion plant. The gasification steam also helps to adjust the temperature in the combustion zone. The crude gas leaving the gasifier is intensively washed in an attached scrubber and the sensible heat is recovered in a waste heat boiler. The wet scrubbing under pressure with a gas liquor containing hot tar eliminates all problems which otherwise particulates may create. The gas is then passed to a crude gas shift conversion reaction which is performed by means of the steam contained in the crude gas, thus eliminating either the expensive cooler-saturator system as often applied for conventional shift conversion processes or the consumption of additional steam. The crude gas is contaminated with sulphur compounds and products originating from coal devolatilization, such as tar, naphtha, etc. The catalyst used is insensitive to these impurities and possesses hydrogenation properties by which the quality of by-products is being improved. By gas cooling, partly in waste heat boiler and partly in air or water coolers, steam and tarry products are being condensed. The resulting gas liquor is at first treated in a gas-liquor separation unit and then dephenolized by extraction with an organic solvent. The gas is then passed through

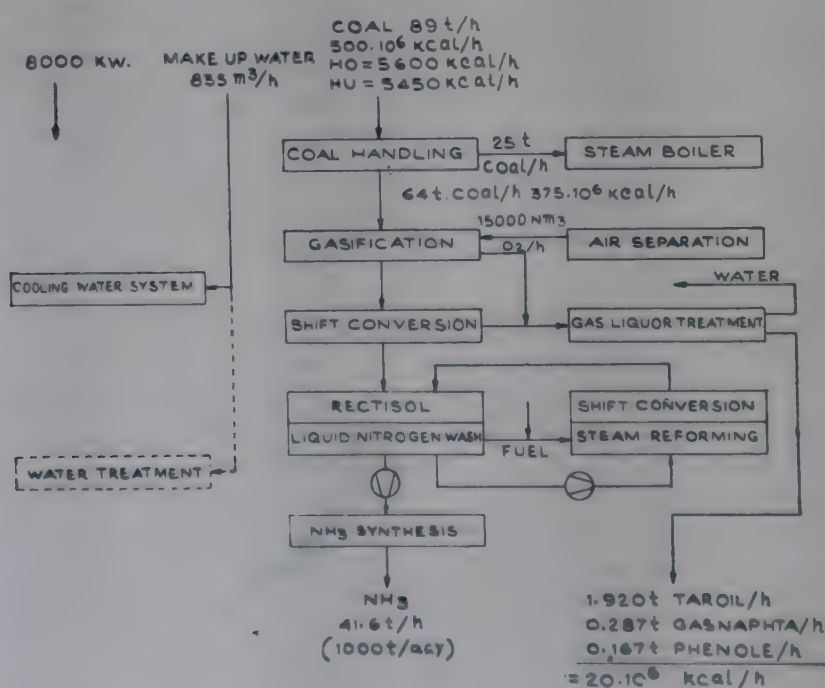


Fig. 2—Coal based Ammonia Plant

a Rectisol unit for removing gas naphtha, unsaturated hydrocarbons, H_2S , organic sulphur and CO_2 , etc. and the purified gas is suitable for all types of synthesis employing very sensitive catalysts. The gas now enters into a liquid nitrogen wash for the removal of CH_4 and CO and is now suitable for ammonia synthesis. The methane fraction separated in the gas separation section and which consists of 70% CH_4 and 25% CO is compressed to 28 atm and then reformed (in a tabular reformer) by the steam-reforming process with a downstream shift conversion. The reformed gas enters the Rectisol plant as an additional feed stream.

Lurgi have a variation of the above scheme, in which the methane fraction is used as feed for an already existing gas or naphtha based ammonia plant. In this example, the coal-based ammonia plant produces 1000 t/ NH_3 /d and the methane fraction together with additional fuel gas available as off-gas from coal gasification can supply feed and fuel for a 600 t NH_3 /d plant.

In both the above process schemes, by-products, like tar, tar oil, gas naphtha and phenols, are manufactured. Lurgi has developed a process to produce a single product known as crude gas reforming process. It enables complete reforming of methane and all organic components still present in the gas downstream of gasification. The steam-containing crude gas containing methane and tarry products from pressure gasification is the feed, which is reformed to synthesis gas; this process requires additional oxygen.

Below (Table 1) the ammonia production cost is evaluated based on German conditions of investment and manpower costs. The result is that in today's market condition ammonia from coal is competitive with the same from naphtha.

The authors has also indicated that Lurgi pressure gasification process offers an efficient route to convert coal into valuable fuels and products followed by a series of processes in such a manner that the various components of the gas and by-products are utilized in an optimum way, viz. (i) H_2 is used for ammonia production, (ii) $\text{H}_2 + \text{CO}$ for methanol or liquid hydrocarbon production, (iii) CH_4 is then available as pipeline gas or feed for other processes, (iv) tar, tar oil, naphtha and phenols for by-product ammonia from gasification.

In the next paper⁴, E. K. Goeke of Koppers explained the coal dust gasification technology, which is based on partial oxidation of coal dust in a flame. Developed as early as 1952, a number of plants are now in operation in the different parts of the world. In this technique the coal dust and the gasification medium, say oxygen, are homogeneously mixed and passed into an empty reaction chamber through a special burner. Immediately after entering the chamber, reaction takes place spontaneously under formation of a flame with temperatures in the core more than 2000°C. Coal dust particles and oxygen move concurrently in the flame, get

4 Status of Coal Dust Gasification Technology by Eberhard H. Goeke, Heinrich Koppers, Essen, W. Germany.

quickly gasified and before the gas leaves the reaction chamber carbon is practically consumed. This means that here a pressure independent water-gas equilibrium is almost attained: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. Due to high temperature all the degasification products and higher hydrocarbons are converted to the components of the homogeneous water gas reaction, with the exception of a very small amount of CH_4 (>0.1 % by vol.). The quality of the gas is similar to that obtained in the partial oxidation of heavy oil (Shell process). The ash is discharged in a liquid form causing no difficulty.

The Koppers-Totzek gasifier (Fig. 3) operates at a normal or slightly increased pressure. It has no movable parts and is provided with a water-cooled double shell in which low-pressure steam is produced and is lined with a highly heat-resistant, refractory material. By special feed screws the coal dust is fed to the burners together with oxygen and, where necessary, small amounts of steam. The larger part of the ash is liquefied in the gasifier and flows off at the bottom through a central opening. On entering the underlying water bath, the liquid slag is granulated and extracted from the water seal by a scraper belt. The granulated slag (size 5-10 mm.) is suitable for making roads and hardstanding areas, etc. and also for the production of cement.

The gas leaves the gasifier at the top and is passed through a waste heat boiler to a mechanical cleaning system (a scrubber and a disintegrator) Electrostatic precipitators can be used to lower the dust content to less than 0.2 mg./ Nm^3 (Fig. 4).

TABLE 1—AMMONIA PRODUCTION COST

		Unit price	DM/t NH_3	
Coal (feed and fuel)	12.0.10 ⁶ Kcal/t NH_3	5.00 DM/10 ⁶ kcal	57.50	
Minus revenue for tar, naphtha, phenols	57 kg/t NH_3	0.10 DM/kg	—5.70	51.80
Utilities				
electric power	192 kwh/t NH_3	0.04 DM/kwh	7.68	
make-up water	20 m ³ /t NH_3	0.10 DM/m ³	2.00	
catalyst and chemicals			1.80	11.48
Operator	52 men/day	55,000 DM/a	9.54	
Staff			2.86	
Maintenance			17.50	29.90
Depreciation and interest				
(15 %p.a., 330,000 t/a) capital investment=175 Mio DM			79.60	79.60
				172.78

In the modern plants the design and operational pressures of the waste heat boilers have been considerably improved. In large integrated single-stream plants to produce 1000 tpd NH_3 , it is desirable to produce high pressure steam suitable for driving the turbines of large turbo-compressors. With the above capacity of

ammonia, 3 gasifiers for operation and one as a standby can be looked upon as optimum. The author claimed that a wide variety of coal with ash content upto 40% and sulphur 5% have been processed. In this process no constituents/ waste products are formed which require chemical treatment. The thermal efficiency of the

gasification unit taking into consideration steam (excluding the l.p. steam produced in the gasifier shell) is around 88%. The carbon gasification is also very high (even upto 99% with a reactive lignite). The time of starting a gasifier is only 45 min. The synthesis gas produced can also be used for the synthesis of methanol, oxo

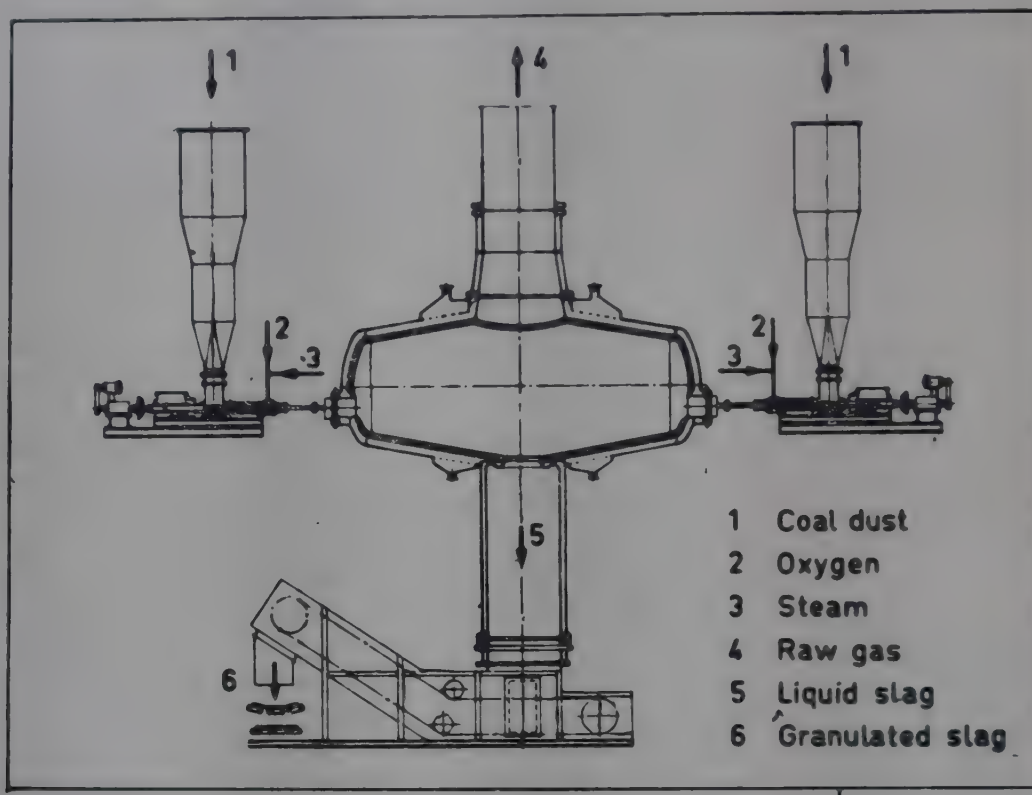


Fig. 3—Koppers-Totzek Gasification

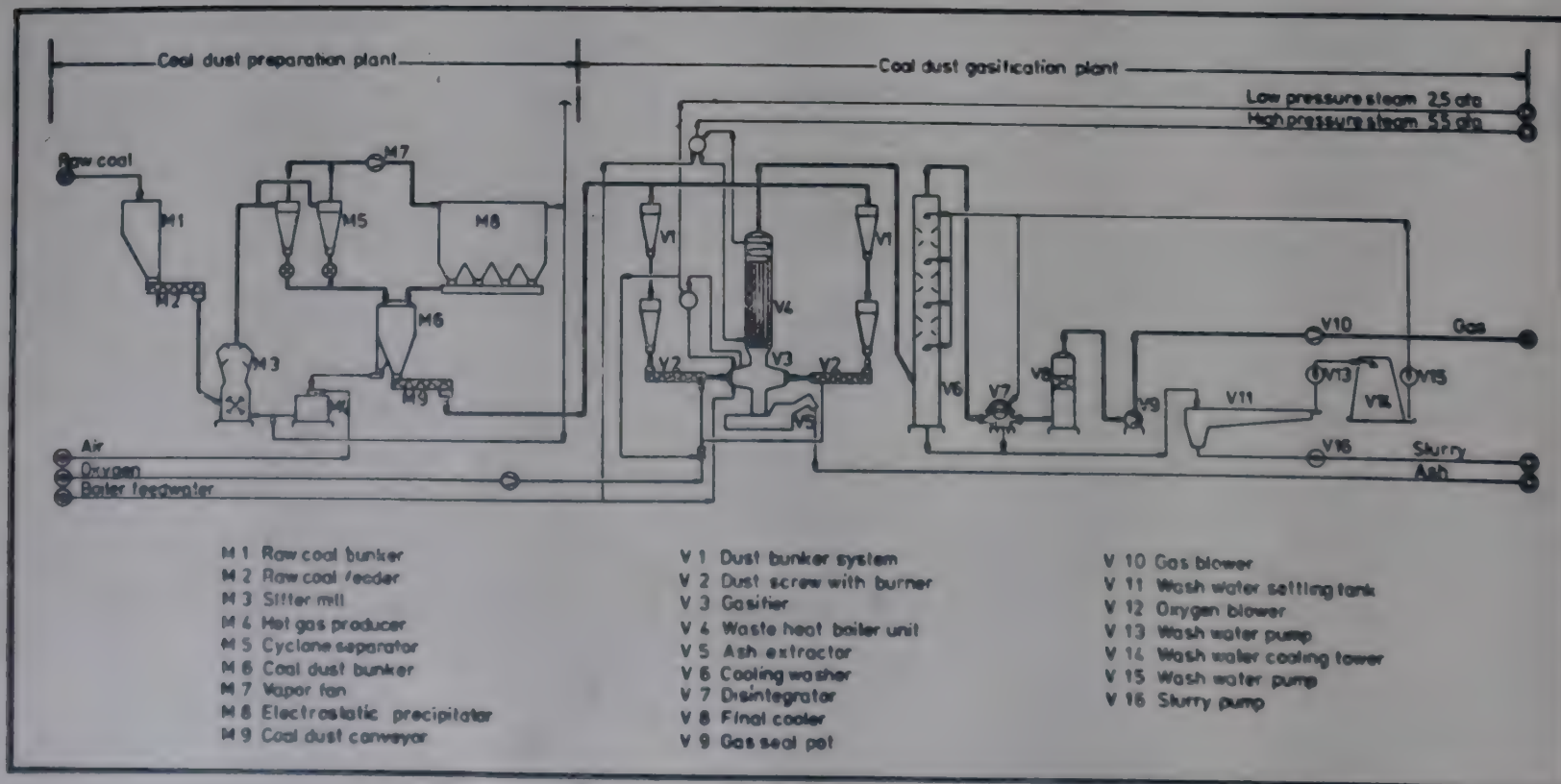


Fig. 4—Koppers Totzek-Gasification Plant

products, methane (SNG) and gasoline (Fischer-Tropsch). The author⁴ mentioned that an integrated coal-based ammonia plant (1000 tpd) now being built at Modderfontein (S. Africa) will go into production in the autumn of 1974.

In discussing the different commercial processes available for total gasification of coal, R. Vaidyeswaran⁵ has pointed the advantages and disadvantages of dust gasification and pressure gasification for the production of synthesis gas. In the Kopper-Totzek, which can utilize coal upto 45% ash, the thermal efficiency is about 75%, which includes the sensible heat of the make gas (26%). The cold gas efficiency is 67% and because of cocurrent flow, the process requires more oxygen to compensate for the varying temperature distribution. The gas contains little methane, no tar and the sulphur is present as H₂S. Purification of the gas is simple.

In the Lurgi process, due to the counter-current flow, thermal efficiency is high and coals upto 45% ash have been gasified. The process has been proved particularly suitable for coals with a high fusion point of ash. Its gasifier is provided with a raking mechanism for gasifying weakly caking (upto caking index 10) coals and the ash is discharged periodically through a lock and chamber at the bottom. The presence of methane in the gas is a disadvantage.

According to the author, while there has not been any significant improvement in Koppers-Totzek or Winkler processes, the high pressure Lurgi process has improved. The crude gas leaving the gasifier saturated with steam is subjected to crude gas shift conversion to bring down the CO content to about 3.5 per cent in two series connected conversion reactors. In the first reactor, the sulphur is converted to H₂S. Multivalent phenols are destroyed and the quantity of tar reduced. In another improvement, the crude gas is subjected to reforming wherein the tar, oil, methane and phenols present in the gas are converted to CO and hydrogen. The residual methane is brought down to 0.5-1 per cent. The by-product is also recycled to the gasifier where the high boiling fraction is utilized for gas production. This has resulted in a saving in the capital cost of the plant for synthesis gas production to the

extent of 4-5%. Another notable development in the high pressure gasification process made in UK and USA is to convert the dry ash removal system to a slagging one where ash is removed as a liquid.

The oxygen plant accounts for 25-30% of the total investment and efforts are continuously being made to avoid oxygen for gasification. The following are some of the processes, which are still in the developmental stage where oxygen is avoided: (i) molten salt process by Kellogg, (ii) CO₂ acceptor process of Consolidated Coal Co. (iii) steam-iron process, (iv) Bigas process of Bituminous Coal Research Inc. None of them has attained commercial importance. Nuclear heat is also under consideration as a source of heat for gasification.

The production and capital costs are lower for the Lurgi process than for Koppers. The cost of production of synthesis gas from coal was higher than that from naphtha by 20-30% with the recent price hike of petroleum coal-based fertilizers will definitely be cheaper.

The production of ammonia from naphtha or natural gas involves about 7 catalytic stages, whereas with coal there are only 2 or 3 catalysts stages—Ht and It CO-conversion and ammonia synthesis catalysts. Messrs C. W. Gent and S. A. Ward⁶ of ICI have outlined some of the important considerations involved in and some suggestions for the design of catalytic stages in a plant including atmospheric pressure coal gasification.

The raw gas produced by the atmospheric pressure gasification of coal is usually purified by the Rectisol process at two pressure levels—30 bar for H₂S and CO removal and 50 bar for CO₂ removal. Sulphur removal down to 5-10 ppm prior to the high temperature CO conversion stage permits a conventional iron/chrome based catalyst to be used in its active form, so catalyst volumes and vessel sizes are minimum with this system. Since the process of CO conversion increases the dry gas volume by 50 per cent, it would be logical to select 50 bar, i.e. the CO₂ removal pressure, thus avoiding the additional gas compression for CO conversion. Although the 30 to 50 bar stage of compression is larger when CO conversion is carried out at the lower pressure, there is no power penalty if the compressor is

driven by a steam turbine. This is because steam has to be added to the CO shift converter at CO conversion pressure to make the shift reaction proceed to the desired exit CO level and if this steam is raised at 50 bar, letting the steam down to 30 bar through a turbine makes extra energy available, which more than compensates for the additional compression power requirement.

Operation at over 30 bar has little effect on catalyst volumes and may well increase the cost of the converter, as a thicker walled vessel is required, with the added disadvantage of the need to limit rapid temperature cycling in start-up and upset conditions in order to limit differential temperature stresses in the wall of the vessel. It is advantageous to have the gas leaving the first catalyst bed near to equilibrium because this prevents a further increase in temperature when flow rates are reduced. This is easier to achieve in practice if the exit temperature is high, e.g. around 520°C, and the cost of a converter for high temperature operation rises if high pressure are considered.

A coal-based ammonia plant with a low temperature CO converter and methanator would lead to conventional synthesis gas having a high concentration of the inerts, methane and argon, whereas the use of a coal gasification process with a nitrogen wash final purification results in a synthesis gas having a very low concentration of inerts methane and argon. In consequence, ammonia synthesis loops using such gases have a number of special features compared with the high inerts loop using conventionally produced synthesis gas. The design of loops and converters for low inert gas is subject to the same conditions and economic assessments to decide pressure refrigeration levels and other important variable as the hitherto more conventional loops.

The synthesis gas after purification by means of a nitrogen wash contain less than 0.01% CH₄ + argon. The CO level can be low (2-3 ppm) but unlike gas purified by methanation can contain 5-10 ppm oxygen. In the high inerts loop, the inerts level is maintained by purging either by (i) solution in the liquid ammonia product or (ii) a voluntary purge taken from the point of highest inerts. In the low inerts loop, the self purging condition is reached when the inerts condition reaches 1-1.5% so it is unnecessary to have any voluntary

5 Synthesis Gas from Complete Gasification of Coal by R. Vaidyeswaran R.R.L, Hyderabad.

6 Catalysts in Coal-based Ammonia Plants by C. W. Gent and S. A. Ward, ICI Ltd. Billingham, UK.

TABLE 2—CHARACTERISTICS OF VARIOUS GASIFICATION PROCESSES

Process	Type of Fuel for Gasification	Size Limits of Fuel Supply for Gasification, inch	Method of Gasification	Gasification Pressure, atm	Quality of Crude Gas before Purification						Approximate Range of Gas Output per Generator, therms/day
					Calorific Value, Btu/ft ³	Sp. Gr.	CO ₂	CO	H ₂	CH ₄	
A. Gasification with Air and Steam											
1. Single-stage producer	Graded coal, Rank 702 to 802 B.S. Swelling less than 4 ash under 15 percent	0.5-2	Non slagging fixed bed, steam and air	1	160	0.9	4	30	12	2.5	2,000-10,000
2. Two-stage producer Gas-Integrale	Graded coal, Rank 802 to 902 ash under 15 per cent B.S. Swelling Index 2	0.5-2	Non slagging, fixed bed; steam and air	1	170	0.8	4	30	15	3	14,000-15,000
3. Single-stage producer	Graded coke	0.5-2	Non slagging fixed bed; steam and air	1	130	0.9	5	30	11	0.5	4,000-20,000
4. Water gas plant	Graded coke		Non slagging; fixed bed; steam and air	1	295	0.5	5	40	50	1	upto 30,000
5. Ruhr gas	Fine high ash coal, ash upto 35 percent	0-5/16	Slagging; suspension, pre-heated air	1	100	0.9	5	20	10	—	17,000
6. Flesch-Demag	Fine, high ash coal	0-5/16	Semi slagging: semifluid bed with steam and air	1	145	0.9	5	30	15	—	9,700
B. Gasification with Oxygen and Steam											
7. Koppers-Totzek	Fine high ash coal, ash upto 40 percent by rank coal	0-5/16	Slagging, suspension, steam and oxygen	1	270	0.7	12	50	35	—	28,000
8. Otto/Rummel	Fine high ash coal, any rank coal	0-5/16	Slagging, suspension, steam and oxygen	1	280	0.7	14	45	40	1	38,000
9. Ruhr-gas	Fine high ash coal any rank coal	0-5/16	Slagging, suspension, steam and oxygen	1	250	0.8	20	50	30	—	34,000
10. Winkler	Fine high ash coal, any rank coal	0-0.5	Non slagging, fluid bed, steam and oxygen	1	230	0.75	28	30	40	—	3,000-75,000
C. Gasification with Oxygen and Steam under Pressure											
11. Lurgi	Small graded coal B.S. Swelling less than 2, ash upto 40 percent	3/32-1 1/4	Non slagging fixed bed, steam and oxygen	25	290	0.7	25	18	40	10	50,000-100,000

purge. The make-up gas efficiencies of the two basic loops are :

- (i) high inerts approx. 2800 Nm³/te of NH₃
- (ii) low inerts approx. 2650 Nm³/te of NH₃

Session 3 : This session was chaired by Sri S. Venkataraman, Adviser (Fertilizers), Union Ministry of Petroleum and Chemicals and Sri Trilochan Singh of Zuari Agro-Chemicals, Goa was the rapporteur. 4 papers were presented.

In the first paper⁷ of this session, the authors have discussed the application of

modern concepts of massive single trains, in plant energy recovery and utilization, centrifugal compression, etc. for the first time in the 3 coal-based units now under construction. While the gas generation section is uniquely adopted for use of coal, the gas processing and purification steps follow essentially same sequences as used in fuel oil processing.

The coals after pulverizing to a fineness of 90% less than 90 microns and dried to an optimum moisture content of 1% will be gasified in an oxygen stream around atmospheric pressure (400-1000 mm. wg.). The powdered coal from the grinding

operations will be collected in a bin under nitrogen blanketing and is conveyed to gasifier section by impure nitrogen stream. The raw gas will then be cooled with waste heat recovery and cleaned to remove all suspended matter—ash, grit and unburnt fuel (Fig. 5). It will be processed under pressure through desulphurization, CO shift reaction, CO₂ removal (with recovery) and a liquid nitrogen wash to eliminate last traces of carbon oxides and to adjust the nitrogen in the mixture. At the beginning, 3 gasifiers with connected trains will be installed, while there is provision for another gasifier as a standby. The generators will have 4 burner head forming a cross in a horizontal plane; each burner is to be served by a powdered coal feed bin and each generator will have 4 burner heads. In the highly turbulent flame generated in the gasifier, the initial combustion of part of the coal dust particles will be rapid with a subsequent slower reaction between the primary combustion products with the carbon frame work left over. The temperatures developed will be sufficiently high (1300-1600°C) to slag the ash, about 60% of which shall drop at the gasifier base while the rest will be carried out up to the shaft of the generator into the waste heat recovery zone.

The gasifier will be lined with a 40 mm. neutral chromite refractory and the metal water-jacketted, in which steam will be raised at 2 ata. The raw gases going up the gasifier shaft at 1500°C will be quenched with a water spray to 900°C which will help to solidify any ash slag. The confining walls of waste heat boiler will be water tubes welded together along their longitudinal axes; the radiation section into which the shaft of the generator will be connected eccentrically is an empty chamber within the water well. Due to drop in temperature and hence gas velocity in this section, a good part of the entrained ash will drop out and collect in a side chamber, which will end up in a water-seal. A common ash extractor will serve the gasifier as well as this water seal.

The cross section of the boiler will be so chosen to approximate as closely as possible to a circle. This would ensure efficient purging in case of emergency. The safety precautions on the systems

TABLE 3—PERFORMANCE DATA OF COMMERCIAL GASIFICATION PLANTS

Process	Winkler	Kopper-Totzek	Lurgi Pressure Gasification
Coal type	Brown coal	Bituminous coal	Bituminous coal
Operating pressure, atm	1	1	20
Input			
Fuel, kg./hr	29,500	1945	1030
Oxygen, kg./hr	14,000	1570	360
Steam, kg./hr	8,350	1050	2200
Gasifier outlet temperature, °C	850	1200	570
Specific consumptions per 1000 Nm ³ /CO + H ₂			
Fuel, kg.	885	660	870
Oxygen, kg.	430	500	300
Steam, kg.	256	207	1790
Power for gasification and compression, kwh	265	260	60
Cooling water, m ³	30	90	150
Products			
Gas production rate, Kcal/m ³ /hr	36 × 10 ⁴	100 × 10 ⁴	800 × 10 ³
Marketable tar and oil, kg.	nil	nil	77
Gas composition, vol. %			
CO ₂	15.7	12.6	30.6
Cn Hm	0	0	0.3
O ₂	0	0.1	0
CO	44.4	51.1	16.2
H ₂	36.0	34.0	42.9
CH ₄	1.6	0.1	9.2
N ₂	0.8	0.9	0.5
Specific gasification rate, therms/ft ² hr	70.6	—	22.6
Specific gasification rate, therms/cuft hr	0.38	1.1	9.0
Steam generated/1000 cft CO + H ₂	0	42.4	22.5
Steam decomposition, %	40.2	29.7	35.7
Per cent C conversion	80	88.6	84

7 Design Philosophy Adopted in FCI's 3 Coal-Based Plants by B. Chatterjee and D. G. Rao, P and D Division, FCI Ltd., Sindri.

have been developed to a high degree of sensitivity and reliability over a period of two decades. Monitoring devices readily detect any starvation of coal dust feeds or oxygen.

The raw gas emerging from waste heat recovery system may contain upto 200 g. of dust per Nm³. It will be subjected to intensive impingement spraying in a cooling washer whereby the temperature of gas will be reduced to ambient and a major part of the dust knocked out into the water. The design will be flexible to take transient high dust contents as well as high inlet gas temperature. The gas will then be sent to a mechanical (Thyssen) washer which would reduce the dust content to 500 mg./Nm³. The quickly opening seal, a safety relief device, will be situated after this washer. A booster will be interposed to augment pressure back to 1000 mm. wg. which will push the gas through a 2-stage electrostatic precipitator (which will reduce dust to 0.02 mg./Nm³) before consigning it to the raw gas holder. The raw gas from the holder will be compressed to the gas processing pressure optimized at 30 ata using a 4 stage steam driven centrifugal compressor. The main design features will be: (i) compressor rpm to be kept low ; (ii) clearance between impellers and casing are meant to obviate any fouling ; (iii) cyclone type separators to be installed after inter-coolers ; (iv) 20 sets of interstage cooler each with a 60-65% gas handling capability will be installed to enable in-service cooling ; (v) spray nozzle will be installed in 3rd and 4th stage barrels for

solvent injection to remove deposits, if necessary ; and (vi) sophisticated trips and alarms will be included to ensure safe operation.

The quality of coal will influence the oxygen consumption as well as raw gas composition throughput, etc.; a high ash content would require a high proportion of inerts to be handled. It would influence the sizes of the grinding mills, feed handling system components, burners, ash handling systems, etc. As an example, when ash content of the feed rises from 15 to 25 %, the coal consumption will go up by 20% and more oxygen will be required to slag out the ash. The ash composition would also effect the operational variables. Since the generator is operated under ash slagging conditions, the lower the ash fusion temperature the lower will be the operating temperature of generator, hence proportionately lower the oxygen consumption. Where refractory ash is to be handled, it will be normal to add fluxing agents to bring down the fusion. The air fractional unit, which will be put in 2 streams: will yield oxygen (98% pure) and synthesis grade nitrogen (99.99 %), besides 2 separate grades of impure nitrogen to be used for pneumatic conveying and blanketing and methanol stripping in decarbonation. The authors have given a scheme to be adopted for steam generation and utilization.

In the early sixties, when the craze for using naphtha as a feedstock for nitrogenous fertilizer was gaining popularity in

this country and elsewhere, it was the Planning and Development Division⁸ of FCI Ltd. which espoused the case for coal mainly through the efforts of Dr. K. R. Chakravorty, who recognized the risks involved in tying up the country's productive capacity in a crucial input fertilizers to the imported petroleum feedstocks. In fact, he argued that the low price of naphtha was artificial—mainly through a subsidy and a part of its price is borne indirectly in the form of higher prices of other products. Coal offers an ideal source of feedstock from the point of view of assured supply under all circumstances and availability at a wide variety of potential production centres, and evaluated in term of real costs to the economy it could compare with liquid petroleum products being an indigenous material, with large employment potential and coal-based plants could generate much larger social benefits compared to imported feed materials.

In giving a brief history of the Korba coal-based fertilizer project, the authors⁹ mentioned that a private party, who had obtained the licence on the lines of recommendations made by a GOI committee headed by Dr. Kane, abandoned the project. So the Government asked FCI to take over and complete the project on a crash basis in 1960. After a tour of the

8 FCI's Experience in Planning and Execution of Coal-based Fertilizer Plants by P. A. Bhaskar Rao, R. R. Poricha and D. G. Rao, P and D. Div., FCI Ltd. Sindri.

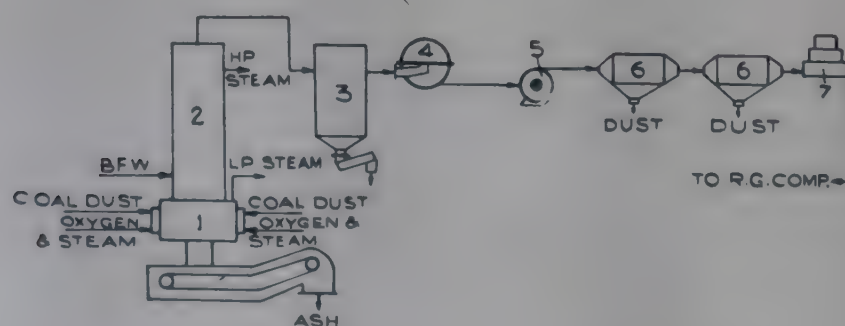


Fig. 5—Schematic Arrangement for Coal Dust Gasification

Legend

1. Coal Dust Gasifier
2. Waste Heat Boiler
3. Cooler Washer
4. Disintegrator
5. Raw Gas Blower
6. Electrostatic Precipitator
7. Raw Gas Holder

M.P. coalfields, the Rajgamar deposits of Korba were selected as a promising source for a 450 tpd ammonia plant. A techno-economic feasibility report was submitted on this basis and considerable amount of ground work was done at the site. Later, license agreements were signed with Koppers for gasification and Montedison for ammonia and urea. Unfortunately Government of India asked FCI to abandon the project on the ground that in view of the development of new naphtha technology it is not advisable to burden the economy with a unit on outdated technology with a significantly higher cost of production. The difficulties and operational problems of the then 2 coal-based units in India viz. Sindri and Neyveli, came handy in argument against coal as feedstock.

Only by 1967, when the magnitude of dependance on imported petroleum feedstock in terms of indirect foreign exchange outgo was realized by the authorities, they constituted a 5-member committee headed by Sri Kasturi Rangan, the then Adviser (Fertilizers) of the Government of India, to visit the coal-based fertilizer plant in Europe and suggest whether such a technology can be adopted in India.

The authors have given the details of the salient data on raw materials and site selection of the 3 coal-based plant, viz. at Talcher, Ramagundam and Korba, each costing about Rs. 120 crores. The plant units are covered with the following licensors and consultants: (i) Koppers for coal gasification, raw gas processing, etc. (ii) Lurgi for the 2-stage Rectisol wash for desulphurization and decarbonation; (iii) Technimont for the ammonia synthesis loop and for the urea group; (iv) Haldor-Topsoe for consultancy on the service steam work, waste heat recovery group, etc.; (v) credit with Technoexport of Czechoslovakia for the air separation and nitrogen separating units and Pregonivest for air and nitrogen compressors; (vi) STC—Sukab deal with Sweden for supply of various stainless steel. Among the indigenous suppliers on whom FCI is dependent are: (a) Bharat Heavy Electricals, Hyderabad and Trichy for centrifugal raw gas, synthesis and refrigeration compressors and drive turbines, (b) Bharat Heavy Plates and Vessels for gasifiers, scrubbers, hortonosphere, stainless steel plants for urea plants, (c) Mining & Allied Machinery for urea scrapers and some conveyors, (d) Test Steel, Ahmedabad for heat exchangers.

In the next paper⁹, S. Ghosh and B. K. Bhattacharyya have reviewed the current status of coal-gasification technology in respect of ammonia plants. The two min processes, Lurgi and Koppers, have been compared. Some of the likely problems one might encounter with such plans have been highlighted to be taken note of in designing future plants in India. Elsewhere in this issue (pp 330-335), this paper⁹ has been reproduced.

In the next paper¹⁰, the authors have described the first high pressure coal gasification plant in the UK, viz. at Westfield (Scotland), which has been in operation since 1960. It is based on the Lurgi gasification process using a low grade, high ash and moisture coal from an adjacent open-cast mine and is meant for supplying town gas to a high pressure transmission grid. At the current capacity, the plant consumes 820 tpd of coal needing 8000 kw electrical supply and 2950 M³/d of water. It has a current capacity of 42 mil. cu. ft. of 475 Btu/ft³-town gas, which is equivalent to an ammonia plant of 320 tpd capacity. The possible application of Lurgi process first received consideration in 1952 and tests were carried out in a pilot plant in W. Germany in the same year as a result of which technical feasibility of the Lurgi process was established. The engineering of the project commenced in 1958.

The processes which make up the Westfield works can be grouped as: (1) gasification (ii) gas purification (iii) enrichment (iv) by-products and (v) ancillaries. The process steps are very similar to the initial steps for ammonia production with the exception of the enrichment stage.

The gas purification process consists of successive removal of tar, oil, ammonia, CO, benzole, CO₂, H₂S and moisture. Tar, oil and NH₃ are removed by a combination fractional condensation and scrubbing in tubular heat exchangers kept at definite separately defined temperature levels, into some of which scrubbing liquor is injected for the absorption of ammonia.

9. Ammonia by Coal Gasification—Factors for Consideration in the Design of Future Plants for India by S. Ghosh and B. K. Bhattacharyya, Indian Explosives Ltd.

10 Aspects of Design and Operation of a Large Scale Coal Gasification Project on a Green Field Site by R. Dars and H. G. Hargreaves

Thus, two condensate fractions are obtained—one consisting of aqueous phase and a tar heavier than water, the other of an aqueous phase and an oil lighter than water; most of the ammonia is contained in one of the aqueous layers. This facilitates the separation and subsequent treatment of these by-products. The partial removal of CO from the gas was necessary for which the well-known CO conversion process, wherein the exothermal reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ takes place over a catalyst around 400°C and above, was adopted the additional CO₂ produced is removed later in the process.

The choice of processes for the removal of CO₂ and hydrogen was a wide including absorption in cold-water, ethanol-amine, hot potassium carbonate, activated potassium carbonate (Vetrocoke) and a low temperature solvent (Rectisol). Of these Benfield hot potassium carbonate system was adopted because the low pressure steam required for it was available from the waste-heat boilers in the gasification section and that the bulk of the H₂S could also be removed along with CO₂. The final removal of H₂S is done by pressure oxide boxes. The gas was then dried in a refrigerated drying system and enriched by butane addition for distribution to the fuel gas grid.

The by-products section was confined to storage of the crude products and preliminary treatment to minimize transportation costs. Tar and oil are separated from the aqueous effluents in the cooling of raw Lurgi gas and disposed of without further treatment. Some of oil produced is used as a washing medium for benzole removal from the raw gas and benzole is stripped from the oil by steam-heating. Crude benzole is sold. Weak ammoniacal liquor (2%) is concentrated to 25% and sold. The disposal of Benfield off-gas was a problem as the concentration of H₂S was insufficient to make oxidation of H₂S to SO₂ and subsequent Clause kiln reaction self-supporting in heat. A plant was, therefore, designed to utilize surplus fuel gas first to burn all H₂S to SO₂ and then to recover some of the sulphur. The dilute phenolic liquor was a permitted effluent for sea discharge.

The commissioning of the plant on schedule, towards the end of 1960, was a technical and commercial success. The

completion of the Stage II construction programme was done in the winter of 1972. According to the authors, processing choices which applied to town gas with its requirement for high calorific value and relatively low purity may not necessarily be identical to the requirement of high purity synthesis gas. The relatively high pressure of gasification used would clearly be helpful in view of the high ammonia synthesis pressure which has to be achieved thereafter. Perhaps the key problem which needs resolving relative to a particular project is the effect of coal-type on the process to be used.

In the discussion, which followed the presentation of papers, some speakers pointed out that pretreatment of coal, like washing, would result in saving in investment in addition to providing better control of quality and middlings could be used in boilers. Some other speakers pointed out that investment would not be reduced as an 100 t/hr washery would not be economical; besides, additional moisture would be introduced which would need energy and equipment for drying. One speaker pointed out that instead of a few large plants at pit-heads it would be worth while to have smaller plants scattered all over the country where adequate coal and power are available.

Session 4: In this session, which was chaired by Dr. V. K. R. V. Rao, Director Institute of Economic and Social Change, Bangalore and a former Central Minister, 5 papers were presented.

In the first paper¹¹, M. C. Verghese and R. P. Cook estimated the world production of ammonia to go up to 90 million tons by 1980 from 47 mil. tons in 1971 and the percentage production of ammonia from coal is expected to double between 1975 and 1980, viz. from 5.8 to 9 mil. tons. Quoting the forecasts (Table 4) made in Sept 1973 before the recent rise in oil prices, they stated the overwhelming predominance of natural gas, which was the cheapest and coal being economic only in special circumstances. From 1971 to 1980, natural gas, coal and fuel gas are expected to increase their share at the expense of naphtha. Though the price of coal is likely to rise because the prices of the competitive fuels will rise, the increase will be much less than for other feedstocks and coal will become more widely used for ammonia manufacture. Depending on the price at which fuel oil settles out, the choice between fuel oil and coal may be a close one. The major advantage of coal is that its use greatly reduces the foreign exchange required.

11. Ammonia from Coal by M. C. Verghese and R. P. Cook, UNIDO, Vienna.

Comparing the feedstock prices, the authors mentioned that for natural gas and coal the lower end of the range (Table 5) corresponds to well-head and coalfield prices outside developed countries and the upper end corresponds to prices in the developed countries. For naphtha and fuel oil, the ranges represent an estimate of the probable stable prices.

On the above figures, natural gas gives much the cheapest ammonia, coal and fuel oil in the same range with naphtha clearly the most expensive; only at a price of \$ 60 a ton or less would naphtha compete with cheap coal or fuel oil. Natural gas prices would have to rise to \$ 1.50 a mil. Btu for fuel oil or coal to compete, while coal at \$ 18 would not be economic in comparison with fuel oil. At the lower end coal prices, the choice between coal and fuel oil would depend on local prices and foreign exchange considerations. The above table (Table 5) is based on the following considerations: (i) plant capacity 1000 tpd of NH₃; (ii) capital cost of complete ammonia plant on an undeveloped site in a developing country is £ 20 mil. (\$ 50 mil.); cost outside the factory excluded; (iii) annual input: natural gas, naphtha and fuel oil = 310,000 tons; annual input coal = 600,000 tons; (iv) ratio of capital costs for the various feedstocks as: natural gas (100): naphtha (113): fuel oil

TABLE 4—ESTIMATION OF AMMONIA PRODUCTION BY FEEDSTOCKS

	Natural Gas		Naphtha		Coal		Fuel Oil		Refinery Gas		Electrolysis		Total	
	%	m. tons	%	m. tons	%	m. tons	%	m. tons	%	m. tons	%	m. tons	%	m. tons
1971	60	26.4	20	8.7	9	4.0	4.5	2.0	4.5	2.0	2	0.9	100	44
1975	62	39.7	19	12.1	9	5.8	5	3.2	3.5	2.2	1.5	1.0	100	64
1980	63	56.7	17.5	15.7	10	9.0	5.5	5.0	3	2.5	1	1.1	100	90

TABLE 5—COMPARISON OF FEEDSTOCKS FOR AMMONIA MANUFACTURE

Feedstock	Price Range, \$	Consumption		Capital Cost, \$		Cost per ton Ammonia (\$)	
		(per ton)		Total (m)	Per Annual ton	Feed-stock	Maintenance and capital
Nat. gas	0.20-0.50/million Btu.	38 million Btu.		46	150	8-19	35
Naphtha	70-90/ton	0.90 ton		52	170	63-81	40
Fuel oil	35-45/ton	1.0 ton		61	200	35-45	47
Coal	5-18/ton	2.0/1.75 tons		92	320	10-32	75

(Annual output = 310 days' output for gas, naphtha and fuel oil; 290 days for coal)

(133): coal (200); capital charges at 20% of fixed capital, plus 3.5% for maintenance.

The problems associated with the use of coal occur in the gasification and gas cleaning plant, arising out of the complex structure of coal with a relatively high oxygen content, a much higher C: H ratio and having ash. The authors, while discussing the 2 proven coal gasification processes, viz. Lurgi and Koppers, pointed out that the major disadvantage of Lurgi is the presence of tars, oils, phenols, etc., which are condensed on cooling with water, thus causing effluent problems; of course the effluent problems have been minimized by recycling the heavy tars and oils to the gasifier and by a crude gas 'shift' reaction. In the Koppers which is a high temperature (1500-2000°C) process, there is no effluent problem and the methane content in the gas is low (0.1-0.2 %). Coal-based plant is capital intensive; it costs almost double that of a natural gas-based plant; experience in Turkey, Greece, Spain and India indicates the average utilization of installed capacities on coal/lignite based plants have been 70-80 % which means that such plants have to be over designed to achieve the desired output.

The authors have presented a scheme for producing 2.5 mil. tons of nitrogen (which is the apparent deficit in the world) using the flared natural gas in strategic locations in countries which have already the infrastructure and gas, such as Trinidad, Tobago, Venezuela, Nigeria, Algeria, Libya, Qatar, Kuwait, Saudi Arabia, Iraq, Bangladesh and Indonesia. 10 identical plants can be built in 2 years' time, each to produce 1000 tons NH_3 and 1500 tons urea per day at a cost of about \$ 100 million. The fertilizers can be produced at less than half the cost compared to today's world prices and sold to deficit countries at fair prices. The oil and gas-rich can cooperate through OPEC or any other organization and such a venture can utilize a wasted resource, flared gas, and supply much needed fertilizers to deficit countries. In the mean time fertilizer deficit countries could be assisted to build more fertilizer facilities based on alternate raw materials, viz. coal, lignite, etc. This idea can be extended to cover phosphates in such countries as Mexico, Morocco, Togo, ARE, Jordan, etc. Setting up of an agricultural input aid fund or an export credit financing fund by an international organization, like World Bank, has been

recommended to support and guarantee exports from the plants mentioned above.

Recalling his earlier study in 1952, Sidney Catell¹² stated that an investigation was carried out by him and other at that time to see if the large coal and lignite deposits of North Central States of USA could be economically used for ammonia production. This investigation indicated that considering freight cost there were areas which might be more economically served by ammonia made from coal than from natural gas. Today most of the ammonia plants in USA are at 1000 tpd level or higher maintaining a more or less stable price, the actual spot price of ammonia being varying between \$ 75 and 90 per tonne. But the growing demand for ammonia and the shortage of natural gas have now raised the ammonia price level to about \$ 120/te.

In the period between 1952 and now considerable work has been done in the gasification of coal but many of the processes were aimed at a synthesis gas which would be readily converted to a substitute natural gas. In the consideration of production of syngas for ammonia the author has used a system where no methane was produced in the gasification segment and has revaluated ammonia production using eastern coal. He concluded that a plant designed to produce 1000 tpd of NH_3 using hydrogen produced by the oxygen-coal gasification at 450 psig followed by 2-stage conversion, 2-stage purification and methanation indicates an estimated capital requirement of \$ 56 millions. (Table 6). Using coal \$ 8/te and discounted cash flow rates of return of 12, 18 and 28 per cent the study pointed out selling prices as \$ 74.57, 92.68 and 111.94 per tonne respectively.

The gasification is the entrained system developed by US Bureau of Mines and other industrial organizations: in this case, it is a single gasifier 6 ft ID $\times$ 17.5 ft. in height with a shell thickness of 1.75, refractory-lined to be operable at 1315 °C. The capital cost of this gasification process is \$ 991,200 and the capital requirements for the complete integrated is estimated at \$ 56 mil.

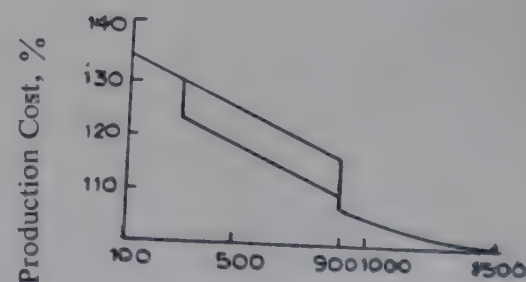
An operating cost of \$ 45.43 per tonne is given by the author considering labour

cost at \$ 5 man-hr. Considering a 12 % discounted cash flow the selling price of ammonia comes to about \$ 74.57 per tonne. (Table 7).

In the second paper¹³ from Heinrich Koppers GmbH, the author, Friedrich Bogner, explained the details of the Koppers Totzek process explaining the factors effecting the economy of coal-based plants. This process is suitable for processing all types of coals. Till now 15 plants with 54 gasification have been built, most of which are still in operation. This process is used for producing synthesis gas, hydrogen, SNG, fuel gas for gas turbines.

The most decisive factors for the economy of an ammonia plant are: location, capacity, process and on-stream factor. The most favourable location of a plant is adjacent to a colliery and simultaneously in a region where the ammonia can be easily disposed of. At Salzgitter (W. Germany), the transportation of liquid ammonia in a 100 km. pipeline between the ammonia and the fertilizer plant proved to be still within economic limits.

While studying the improvement of economy by increasing the capacity of plant and stream, it is found that in the range upto 900 tpd the top line of the double curve (Fig. 6) refers piston compressors with electric motor drive and the bottom line to steam turbine drive. The ascent from 900 tpd is due to the fact that from this capacity, the effective gas volume facilitates the utilization of high pressure turbo-compressors with steam turbine drives also high pressure steam is extensively produced from waste heat.



Ammonia Plant Capacity, t/d
Fig. 6—Improvement of Economy by Increasing Capacity of Each Plant and Stream

12. An Evaluation of Coal as a Source of Synthetic Fertilizer Production by Sidney Katell, Bureau of Mines, US, Deptt. Interior, West Virginia, USA.

13. How to Improve Economics of Coal-based Ammonia Plants by Friedrich Bogner, Heinrich Koppers GmbH, Essen, W. Germany.

The processes of the individual technological stages—gas production, gas cleaning, gas compression, synthesis and energy system—are to be selected according to the local conditions such as raw material and energy supplies, air-water or sea-water cooling system. However, even if the type of coal is changed because of non-availability of the previous type, no difficulty will arise in this process because all types of coal can be processed.

A comparison Figs. 6 and 7 indicates that the production costs of a 300 tpd plant which operates at a yearly average capacity of 90% are approximately equivalent to those of an 1000 tpd operating at only 60% capacity. This fact is not given much consideration. Particularly large-integrated plants require comprehensive expertise regarding operation and maintenance and therefore continuous training of the personnel is absolutely necessary. When operating integrated plants at fluctuating partial loads, frequent troubles and damages inevitably occur, particularly to heat exchangers due to the increased material stresses resulting from temperature fluctuations and damages due to corrosion which occurs when falling short of the dew plant. If a repair requires shut-down of the plant, it is more advantageous to replace the entire unit, immediately put the plant into operation again and to properly clean and repair the replaced equipment in a central workshop.

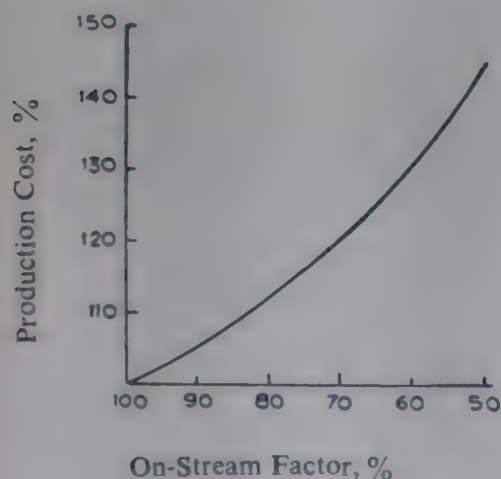


Fig. 7—Effect of On-Stream Factor on Plant Economy

In the next paper¹⁴, S. K. Mukherjee *et al* have analysed the technical and financial implications of change-over of a plant meant for operation with fuel oil to coal. Elsewhere in this issue (pp 309-314) this paper has been reproduced.

In early 1973, the Project Appraisal Division of the Planning Commission

undertook a detailed study¹⁵ of the relative imports of different technologies of production of urea was undertaken. Production of hydrogen from natural gas and electrolysis of water was not considered. Towards the end of 1973, when the price of naphtha rose from \$50 to \$ 130 per te, the cost of urea from naphtha based plants became exceedingly high. So in early 1974 a revised study was understood without taking naphtha into consideration (Table 8). The price of coal varied substantially from one place to another and the price of fuel oil was fast changing and thus the ratio of the capital cost of coal-based to a fuel-based plant has increased to 1:2 compared to 1: 1. In the first instance the author worked out the cost of urea production to different prices of coal and then worked out the price of fuel oil at which the cost of production of urea in fuel oil based plant would be the same—this he termed as equicost (Table 9). The interesting finding which emerged from this exercise is that the cost of production of urea would be substantially lower than its current import price which is over \$ 200. It can be seen that the cost of urea corresponding to the cost of coal at Rs. 70/- is Rs. 787/- On the other hand, if it were to be produced in a fuel oil based plant, the price of fuel oil has to be Rs. 503 to get the same cost. The cost of fuel oil is actually around Rs. 540-600 so at the current price of fuel oil, coal based plant should be preferred. The author has already assumed that a coal-based plant will cost 20% more than a fuel-based plant of the same capacity and its construction will take one year more.

Session 5: In this session, which was chaired by Dr. G. S. Sidhu, Director Regional Research Laboratory, Hyderabad, 2 papers were presented. In the first paper¹⁶, presented by Sri M. M. Sen

14. A Case Study of Design of a Fuel Oil Based Plant Keeping in View the Possibility of Eventual Change-over to Coal as a Feedstock by S. K. Mukherjee, B. Chatterjee, T. R. Ardhanari and D. N. Bhowmik, FCI Ltd. New Delhi
15. The Economics of Coal-based Urea Production by T. L. Shankar, Planning Commission, Government of India, New Delhi.
16. Development Work on Complete Gasification of Coal at CFRI by D. K. Biswas, A. Majumdar, M. M. Sen and S. K. Das Gupta, Central Fuel Research Institute, Dhanbad.

(CFRI), the authors described the pilot plant development carried out in the Central Fuel Research Institute in the field of complete gasification of coal for various industrial and domestic uses and discussed the typical test results and salient features of pilot plant experiments carried out for studying the steam-oxygen gasification characteristics of Indian coals in suspended bed gasifier operating at atmospheric pressure and in fixed bed gasifier operating at elevated pressures for production of synthesis gas and town gas. Elsewhere in this issue (pp 315-329), this paper has been reproduced.

In the last paper of this symposium, Dr. V. R. S. Arni described¹⁷ the 2-stage pressurized fluidized bed process for gasification of coal developed and patented by the Union Carbide Corporation. This process is best suited to low rank high ash coals and has been selected under the Joint Programme of the U.S. Office of Coal Research, the American Gas Association and the Columbus Laboratories of the Battelle Memorial Institute. The process is expected to be ready for commercialization by 1976. The early emphasis on coal gasification in USA was due to (i) dwindling resources of natural gas which served over 30% of USA's 1970 energy requirements and (ii) the rapid growth of environmental legislation which seriously threatened the direct use of coal (which contributed about 20% of total energy in 1970).

According to the author, the first generation processes are the Winkler, Lurgi, Koppers Totzek, the SNG processes (nearing commercialization) of Lurgi, Bituminous Coal Research's 2-stage BI-GAS-process and U.S. Bureau of Mines' 1 stage SYNTHANE process. The economic problems of these processes are (i) the high investment in oxygen plants and oxygen production costs, and (ii) dilution of product gas by CO₂ production.

The second generation processes, now under widespread study, attempt to substitute oxygen usage by other means of heat supply. These processes are : (i) M. W. Kellogg's molten salt reactor process where circulating molten sodium carbonate supplies the heat of reaction, with ungasified carbon carried by the melt to an

17. The Union Carbide Agglomerated Bed Process and Concepts in Coal Gasification by V. R. N. Arni, Union Carbide India Ltd., Bombay.

TABLE 6—TOTAL ESTIMATED CAPITAL REQUIREMENTS AND OPERATING PERSONNEL

Unit	Cost, \$	Per cent	Estimated Number of Operators per Shift
Coal preparation	915,300	1.6	2
Gasification	991,200	1.8	1
Dust removal	226,200	0.4	—
First stage shift conversion	477,200	0.9	1/2
Heat recovery No. 1	841,800	1.5	1
First stage purification	4,050,100	7.2	1
Second stage shift conversion	236,400	0.4	1/2
Heat recovery No. 2	422,700	0.8	1/2
Second stage purification	1,610,800	2.9	1/2
Methanation	485,700	0.9	1/2
Synthesis gas compression	5,985,900	10.7	1/2
Synthesis unit	10,174,400	18.1	2
Sulphur recovery	450,000	0.8	1
Oxygen plant	7,494,000	13.4	2
Steam and power plant	6,736,000	12.0	2
Plant facilities	3,082,400	5.5	1
Plant utilities	4,418,100	7.9	1
Total construction	48,598,600	86.8	17
Initial catalyst requirements	589,600	1.0	
Total plant cost (insurance and tax gases)	49,188,200	87.8	
Interest during construction	3,935,100	7.0	
Subtotal for depreciation	53,123,300	94.8	
Working capital	2,936,700	5.2	
Total investment	56,060,000	100.0	

external reheat section where the carbon (still in the molten salt) is burnt in air to raise the temperature of the melt; (ii) Consolidated Coal Cos' CONSOL process, where a circulating stream of dolomite reacts with CO₂ in the gasifier to produce heat, and the outgoing MgO.CaCO₃ stream calcined outside the reactor to reproduce

CaO.MgO, and (iii) the Union Carbide Agglomerated Bed process.

The Union Carbides is a 2-stage pressurized fluidized bed process (Fig. 8) in which agglomerated, free-flowing and spherical ash particles circulate in a practically close-loop; being formed and heated up

in one-stage—burner or-combustor—and releasing a part of their sensible heat in a second stage, the gasifier. The ash agglomerates, in effect, become an inert heat transfer medium for sustaining the endothermic steam-carbon reactions of the gasifier. The use of this inert medium enables air to be used in place of oxygen,

TABLE 7—DISCOUNTED CASH FLOW, 12 PER CENT

Capital investment	56,060,000
Less present value of working capital recovered in 20th year, = \$ 2,936,700 × 0.1037	304,500
Investment	55,755,500
Annual cash flow required at 12% 20 years	7,464,900
Less depreciation	2,656,200
Net profit	4,808,700
Gross profit (Federal income tax at 50% of gross profit)	9,617,400
Operating cost	14,991,800
Total	24,609,200

Annual ammonia production = 1,000 × 330 = 330,000 tonnes
Selling price = \$ 24,609,200 ÷ 330,000 = \$ 74.57 per tonne

TABLE 8—COMPARATIVE COST OF COAL-BASED AND FUEL OIL-BASED PLANTS ON THE BASIS OF REVISED PRICES

Basis of Cost Estimates	Coal-based Plant	Fuel Oil-based Plant
Capital cost as Adjusted, mil. Rs.	998.6	820.6
Gestation Period	4 hr.	3 hr.
Production Build-up	50, 75, 90%	50, 75, 90%
Life of Plant	15 hr.	15 hr.
Rate of Discount	10%	10%
Rate of Foreign Exchange	Rs. 7.5/\$	Rs. 7.5/\$

15. The Economics of Coal-based Urea Production by T. L. Shankar Planning Commission, Government of India, New Delhi.

TABLE 9—COST OF COAL-BASED UREA PRODUCTION AND EQUI-COST OF FUEL OIL, RS.

Price of Coal Rs/te	Estimated Cost per tonne of Urea	Equi-cost Price of Fuel Oil
90	767	480
70	787	50
80	807	526
100	847	572
120	885	618

for combustion and yet not dilute gasifier products through the introduction of nitrogen so significant levels of carbon dioxide. In the burner 60-100 mesh char particles are burnt with air when the ash in char undergoes incipient fusion forming agglomerates. This self-agglomeration or pelletisation process yields a readily circulatable, inert heat transfer medium. The hot agglomerated ash from the burner enters, the gasifier vessel at a suitable point and after parting with a part of the sensible heat to sustain the endothermic reactions, is recycled back to the burner for reheating. The agglomerated ash is steam-lifted to point A (Fig. 9) and because of the state of the solid/gas systems in the gasifier, rains down in a net downward direction. This enables a counter current operation and facilitate sinter removal from the bottom of the gasifier. Superheated steam principally enters at point B below the fluidized bed distributor plate and acts as a transport medium for the sized coal feed entering at the bottom of the gasifier (Fig 9), known as the stripping zone. The coal size fed to the gasifier determines the char size going to the combustor as coal conversion leads to a char sponge with size about as fed coal. Gas velocities in the stripping zone are

about the incipient fluidization velocity of the sinter to permit the aforesaid downward movement of the sinter and its discharge. The fluidizing medium in the upper section of the gasifier is a combination of steam and syngas. Ash agglomerates for recirculation and reheating in the burner leave at point D and are pneumatically transported to the burner using a slipstream of product syngas.

In the burner operational conditions are needed to ensure that (i) a large surface of coal particles are exposed to air to achieve rapid combustion and (ii) temperature uniformity such that $\pm 50^\circ\text{F}$ is maintainable so that while ash softens and agglomerates, actual fusion or slagging do not occur. It is important to note that temperature has a profound influence on the ability to hold the solid-gas system in the burner in a stable condition.

Fluidization-bed conditions are necessary in the upper section of the gasifier because (a) dilute suspensions permit rapid heat and mass transfer at the steam-carbon interfaces (b) a means is provided for the net downward movement of heavier ash agglomerates and its removal from the gasifier. The amount of ash-

agglomerates in circulation is quite large in the Union Carbide process, the ratio of ash in circulation to coal feeds being 20-30 and could be as high as 40. In the Battelle programme which involves coal utilization at the rate of 25 tpd, the ash in circulation is about 20 tonnes. This circulation has two advantages viz. in the burner it acts as a heat sink to hold down and control temperatures and it brings about dilution of the coal particles such that even caking coals do not swell and sticktoform agglomerates.

Union Carbide have developed conceptual integration schemes related to different environments. Because of the unique characteristics of the self agglomeration process in producing a fly ash free from flue gas, it is eminently possible to obtain electrical energy from the hot exit stream by means of a gas turbine driven generator, which will be sufficient to drive the burner air compressor. They are also studying conceptual schemes based on their above developing technology of utilizing the syngas stream to produce electric power, SNG, bulk organic chemicals and inorganic industrial products, such as ferro-alloys calcium carbide electrolytic metals, where electrical energy

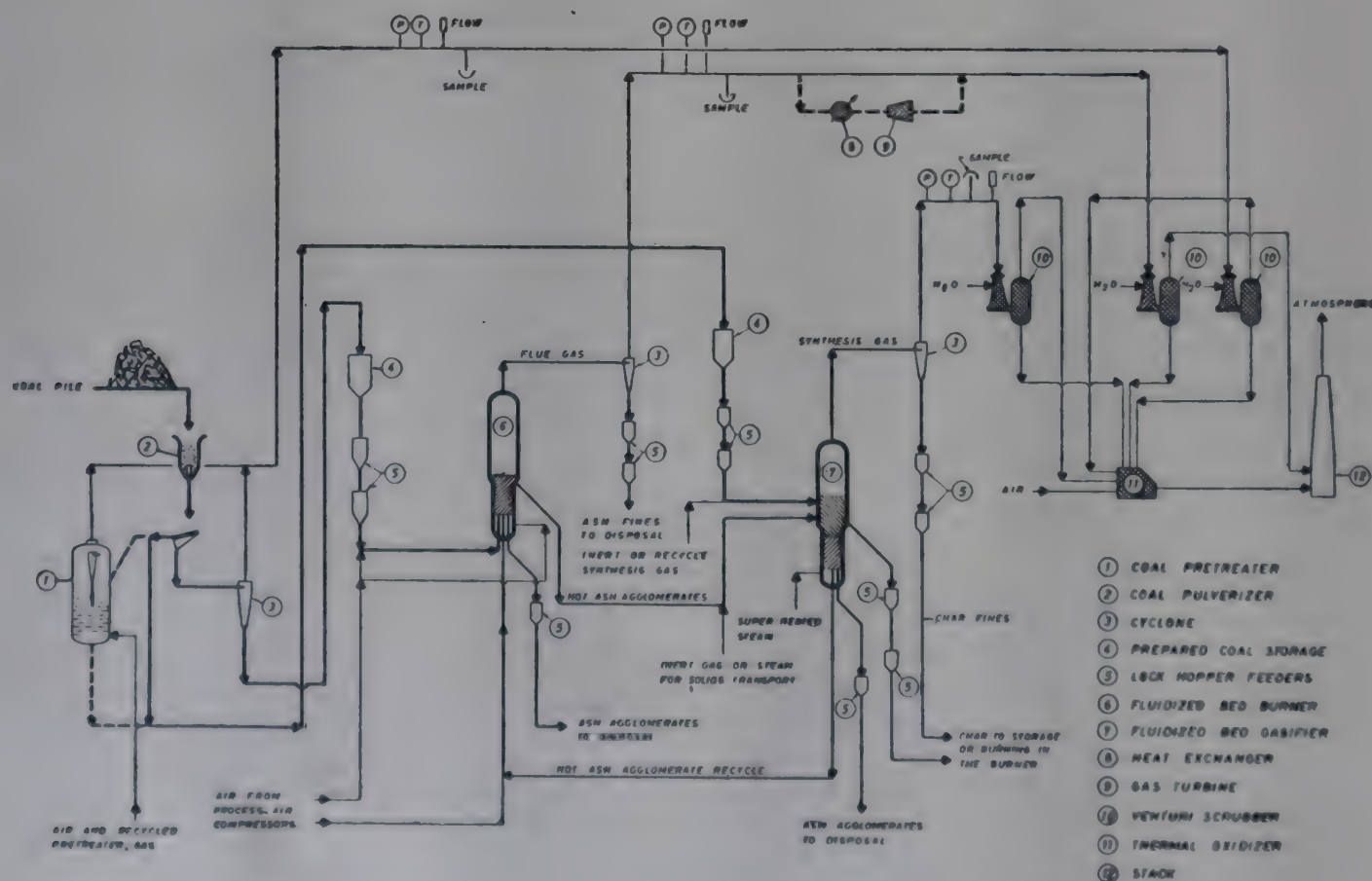


Fig. 8—Simplified Flow-sheet Process Development Unit for Self-Agglomerating Gasification Process

inputs are of equal magnitude to raw materials requirement.

Incidentally, the Dr. Arni mentioned Union Carbide's current process development programme or setting up a 150 tpd R and D plant in Bhopal for studying

Indian non-coking coals to obtain kinetic data and evaluate burner/gasifier flow systems. The objectives are (i) to evaluate the suitability of M. P. and other low rank, high ash coals taking into consideration their caking and ash fusion characteristics, etc. (ii) study the suitability

of locally manufactured refractories or need for modifying burner/gasifier design (iii) simplify materials handling problems including that of coal as a slurry from pit heads and (iv) obtain scale-up data for engineering large commercial plants.

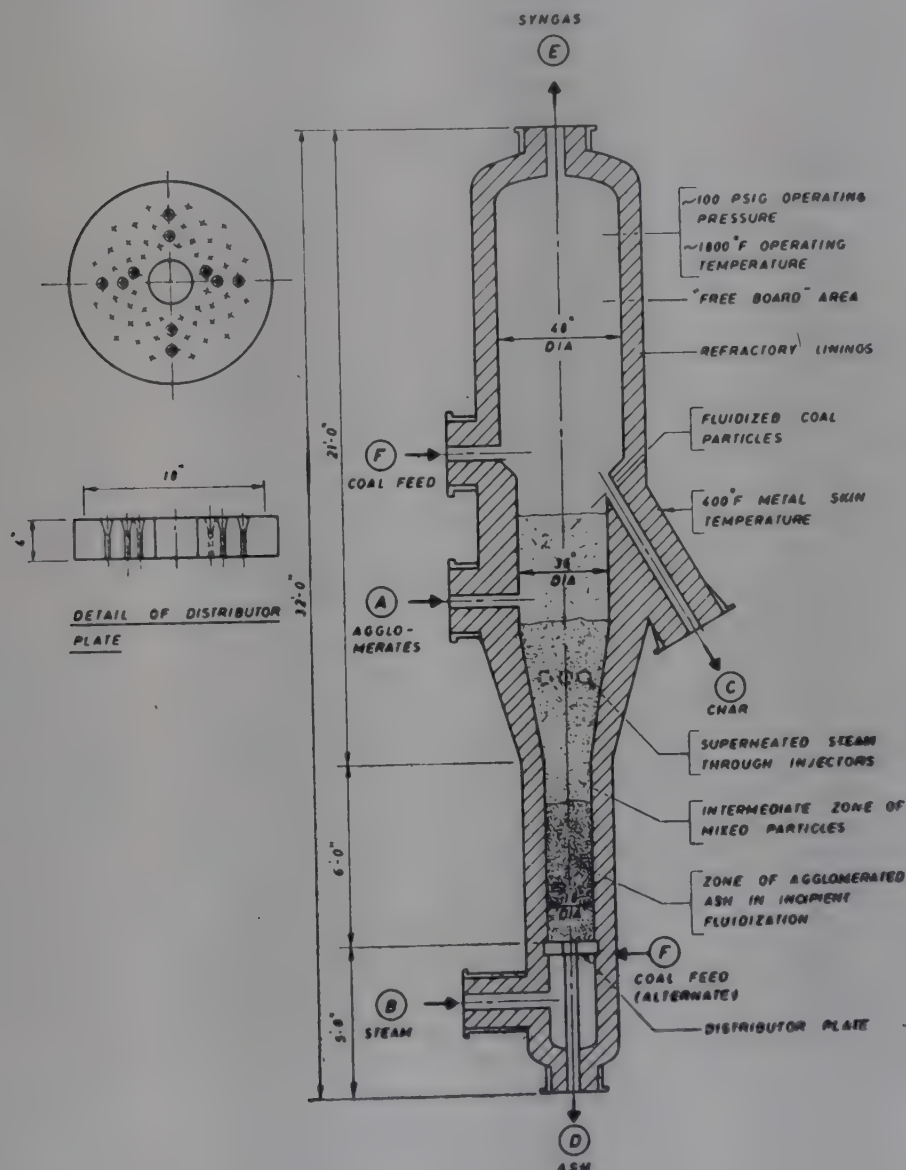


Fig. 9—Gasifier Vessel Construction

Notes & News

Effluents Treatment at F.C.I., Namrup

According to the standards laid down, a stream containing more than 1-2 ppm of ammoniacal nitrogen, is considered unsuitable for pisciculture. With the coming up of large sized nitrogenous fertilizer plants, river pollution problem is getting a bit accentuated due to ammoniacal discharges in the areas where these plants are located. The Namrup Unit of FCI, which has a capacity of producing 200 tpd of ammonia, 167 tpd of urea and 304 tpd of ammonium sulphate, is one such example. The problem is likely to be aggravated further at Namrup with the coming up of the expansion project which will add 600 tpd of ammonia and 1,000 tpd of urea to the existing capacities. The designers of the plant had indicated at the time of commissioning, that the discharging effluents from the three main plants, viz. ammonia, urea and sulphuric acid, will not exceed the tolerance limits to cause river pollution. But the problem of pollution, as it stands today, will become still alarming with the expansion project. So a suitable scheme has to be found out for treating the effluents and discharges before entering into the river. The P & D Division of FCI at Sindri, after a thorough study of the problem, has suggested an integrated scheme to take care of the effluent's problem of both the existing and the expansion plants. The entire scheme, consisting of building, stripping and ion-exchange sections, will cost around Rs. 4 lakhs. The scheme suggested is as follows : (a) A stripping plant is to be installed for treating 25,000 kg./hr of condensate effluent containing 2-4 per cent ammonia from the expansion urea plant. The harmful ammonia in the condensate shall be stripped off in the steam stripper and ammonia vapours coming out from the top of the stripper shall be neutralized with sulphuric acid to form ammonium sulphate which in turn will get processed in the existing plant. The effluents coming out from the bottom of the stripper are expected to get sufficiently diluted with the discharge of the entire factory so as not to be a problem any longer. Alternatively, if the harmful ammonia is still beyond the tolerance limit, the stripper discharge shall be further treated in an ion-exchange unit before discharging into the river.

(b). The effluents coming out from the existing urea plant are of the order of 80 cu.m./hour having a concentration of 1,000 ppm ammonia on an average. These effluents will be treated in an ion-exchanger unit, where harmful ammonia shall be selectively absorbed on a cation exchange resin. The ammonia shall, however, be recovered as ammonium sulphate during the process of regeneration of the resin with sulphuric acid. The effluents after their passage through ion-exchangers would contain a maximum of 50 ppm of ammonia.

As a precautionary measure, the effluents from the stripping unit and the ion-exchange plant after removal of ammonia shall be pumped into a big delay pond within the factory boundary wall to further regulate the discharge into the river. Thus, the scheme when implemented would make the effluents completely innocuous.

[*Fert News*, 18 (10) (1973), 27]

Hydrogen & Synthesis Gas Production By Partial Oxidation

Two processes, widely used for the production of synthesis gas and hydrogen, are steam reforming of light hydrocarbons and partial oxidation of a wide range of oil products. Partial oxidation process, however, is favoured due to its applicability to heavy residual oil products and the increasing scale of production. This process can utilize a number of feedstocks ranging from natural gas to propane asphalt. Presently, the partial oxidation process is in use for a number of industrial applications, such as ammonia synthesis, methanol synthesis, oxo-synthesis, hydrogen and reducing gas generation. The process is based on the Shell gasification process, which is in operation in 19 countries for the manufacture of synthesis gas for ammonia, methanol and oxo-alcohols synthesis. The partial oxidation process favours well in the development of large scale plants. The partial oxidation route has not only made inroads into the manufacture of ammonia, methanol and hydrogen but has also been very successful in the manufacture of oxo-syn gas. The Shell gasification units have an excellent maintenance removing record. The process also curtails the pollution

abatement by the last traces of the contaminants like HCN and H_2S in the waste water. Another point of credit which goes in the favour of the partial oxidation units is the flexibility of utilizing by product steam for any desired purpose. A number of developments have now been made in this process since its introduction. Broadly, these are : reduction of gas compression cost and thus saving some 600 kWh per ton of hydrogen ; increase of reactor production capacity ; and improvements in the disposal of by-product carbon and also the use of waste-heat boilers for recovery at high steam pressure. It is strongly contended that developments in ecology, fuel availability and scale of industrial plants will favour the use of the partial oxidation process and its further development.

[*CEER* 5 (12) (1973), 22]

Lurgi Process for SNG from Coal

The conversion of coal into methane is undoubtedly a difficult task. But the pressure gasification process developed by Lurgi for the treatment and purification of gases originating from coal is capable of meeting the far reaching requirements of energy supply. High-ash young bituminous coal is converted in a Lurgi pressure gasification plant at 26 kg./cm.² into gas which is then purified in a Lurgi Rectisol plant. The SNG from this plant meets all specifications for natural gas and has a calorific value of 972 Btu/scf. The overall process plant consists of five different steps which have been specifically developed for gas manufacture from coal.

Pressure Gasification : The coal is pre-heated and dried, and as it moves down it meets rising gases and is heated up, devolatilization commences and from a temperature of 1150 to 1400°F onward, devolatilization is accompanied by gasification of the resulting factor for the resulting char. The product of gasification is a mixture of various components, mainly CO_2 , CO, CH_4 , H_2 , H_2O , and products of coal carbonization, such as tar, oil, naphtha, phenols etc., plus sulphur compounds and other impurities. The minimum residence time of about one hour is maintained for good performance of the reactions at the temperature level of 1400 to 1600. The crude gas leaves the

gasifier at temperatures between 700 and 1100°F depending upon the type of coal. It contains carbonization products and so is passed through a scrubber where it is washed by circulating gas liquor and then cooled to a temperature at which the gas is saturated with steam. At higher boiling tar fractions are condensed. The wash water contains tar to which the coal and ash dust is bonded. The steam saturated gas is passed to a waste heat boiler in which waste heat at a temperature of 320°-4 to 360°F is recovered. The gas liquor condensed in this boiler is pumped back to the scrubber and surplus gas liquor is routed to a tar-gas liquor separator. The mixture of tar and dust is returned to the gasifier for cracking and gasification. In the gasifier about 80 per cent of the coal fed is gasified and the balance of 14%, which is mostly carbon, is burned in the combustion zone with oxygen.

Crude Gas Shift Conversion : The resulting H_2/CO ratio of the gas from the gasifier is not suitable for subsequent methane synthesis. Therefore, a shift conversion reaction ($CO + H_2O \rightarrow CO_2 + H_2$) becomes necessary to adjust the H_2/CO ratio. This task is fulfilled by employing Comox catalyst. The major feature of the crude gas shift is the use of undecomposed steam in the crude gas downstream of the waste heat boiler in the gasification section for the performance of the shift reaction. However, the crude gas is contaminated with sulphur compounds and carbonization products. The catalyst which possesses hydrogenating properties, gets the carbonization products hydrogenated and especially the gas naphtha is desulphurized. This reduces the output of the gas liquor considerably.

Rectisol Gas Purification: Purification of gas from coal gasification to a degree of purity as required for synthesis processes is a difficult task due to the large quantities of impurities and variety of these impurities. The Rectisol process developed for purification is a physical gas absorption process, which uses organic solvents preferentially methanol at low temperatures between approximately + 30°F and - 80°F. Crude gas is contacted counter-currently with the solvent in a trayed absorption column and the spent solvent is regenerated by flashing and subsequent stripping or reboiling in a desorption column from which it is recycled to the top of the absorber. The Rectisol unit consists of three sections a, b and c to cover the

above process. Section (a) is the prewash for the removal of gas naphtha, unsaturated hydrocarbons and other high boiling gas impurities. Section (b) is for CO_2 removal and for the removal of H_2S and COS . In section (c) the last portion of the CO_2 is removed and the gas is also dehydrated. The gas leaving the Section (b) is the syngas having the purity required for the methane synthesis.

Methane Synthesis : The $(CO + H_2)$ component of the gas leaving the Rectisol plant and in case also a portion of the CO_2 is still left in the gas have to be converted to methane synthesis. The process which is yet to be operated commercially will, however, be able to produce SNG of 970 Btu/scf.

Lurgi Phenosolvan Process : Gas leaking from the coal gasifier contains a fairly large amount of steam in condensed form. The resulting gas liquor remains in contact with coal carbonization products and thus contains components which are soluble in water, mainly phenols, ammonia and fatty acids. The Lurgi Phenosolvan process removes the phenols and the ammonia. The purified effluent contains not more than 20 ppm phenols and not more than 60 ppm of free ammonia. This effluent can further be processed in biological water treatment plant, so that finally, effluent leaving the plant meets either the regulations for the disposal of waste liquor or can be used as raw water.

[*Lurgi Process Route to SNG from Coal*, Bull. Issued by Lurgi India Ltd. New Delhi]

Coal Liquefaction Technology

Utilization of coal and the present search for energy sources calls, among other things, for the gasification and liquefaction of coal. The Kyushu laboratory of the Agency of Industrial Science and Technology has developed a new liquefaction process called Solvolysis. The laboratory has been doing work on this process for some years. The process, which is a result of research and development work with a pilot plant, can be compared with the existing two liquefaction processes. Moreover, the process is simple and cheap.

The new coal liquefaction process has the following features : Two parts of asphalt are added to one part of coal and the mixture is heated to about 400°-450°C, whereupon numerous crystalline liquid microbeads are formed in the asphalt. The

asphalt containing the crystalline liquid completely dissolves the coal and forms modified pitch at a ratio of two parts of pitch to one part of coal. The remaining distillates obtained is similar to kerosene or gas oil. The crystalline liquid microbeads are capable of completely absorbing the ash content in the coal, depending on the way in which they are formed. It is possible to obtain ash-free pitch (at a ratio of 0.9 against one part of coal) by separating the ash containing microbeads. Distillates (one part) are added to this. The product obtained here is a clean heavy fuel oil (2.9 parts). The ash-containing crystalline liquid microbeads can be used as a special carbon material while the sulphur in the coal and asphalt can be removed during the separation of beads. The final sulphur content can be reduced to less than 1%.

One of the present two coals liquefaction processes called as direct hydrogenation liquefaction process involves making a paste of coal by adding mixed oil to coal and then adding a catalyst for reactions with hydrogen at high temperature and pressure. The other process consists of adding a solvent to coal, then adding a catalyst to the mixture for reactions with hydrogen at high temperature and pressure. As only the portion liquefied through these reactions is extracted, this process is called extractive hydrogenation liquefaction. But both of the presently available processes involve high pressure and require the use of catalysts and hydrogen. Removal of ash is further a major problem. However, the new process has made possible the removal of ash completely, and does not require the use of expensive hydrogen, catalysts and high pressure equipment, leading to considerable cost savings. In addition, as the solvent not only petroleum-derived asphalt but also coal-derived coal tar can be used.

[*CEER* 6 (4) (1974), 40]

Fluorine Recovery from Phosphoric Acid Process

The effluents from a phosphoric plant require to be treated to remove fluorine from the effluent gas : phosphate ore usually contains an appreciable amount of fluorine, between 3 and 4.5 per cent by weight. The fluorine is released when the rock is reacted with acids. The distribution of fluorine depends both on the rock and the operations. There are number of factors that can affect the distri-

bution of fluorine compounds : the sodium and potassium content of the rock, which tend to precipitate fluorine as fluosilicates ; the reaction temperature which, if increases, produces more fluorine in the gas phase; and the concentration of phosphoric acid produced, which increases the quantity of fluorine produced as it increases in concentration. In the U.S., out of a total of about 1.2 million tons of fluorine released in a year, less than 100,000 tons/year is presently recovered. Fluosilicic acid, probably the major product, can be recovered from the phosphoric acid process by methods now in commercial use, equivalent to 1 million tons/year of fluorspar. Keeping this application in mind, Reed Process Co. of Milling, NJ developed their RHT process for separating hydrofluoric acid from fluosilicic acid. Main features of this process are flame hydrolysis and high temperature silica separation. The fluosilicic acid fed to this process is recovered by scrubbing it from the vapour from the phosphoric acid concentrators. The reactor consists of a cylindrical furnace and is lined with high alumina refractory. Vapourised fluosilicic acid and air are mixed with fuel in a burner of special design, the fuel can be natural gas, LPG, or vaporised No. 2 fuel oil. Mixing is controlled so as to obtain silica of the proper particle size for its easy separation.

Silicon tetrafluoride hydrolyses at about 2400°F, the reaction being rapid and complete. The reactor effluent is cooled only upto 1200°F. Separation of silica at this temperature, however, requires efficient agglomeration prior to mechanical separation by cyclones. After the removal of silica, the reaction gases are further cooled by air exchange and allowed to enter a scrubbing tower. Here hydrogen fluoride is absorbed in water. The gases are further passed through a limestone packed tower which removes the last traces of fluorine before release. Hydro-fluoric acid from the concentrator is contacted with sulphuric acid in a Karbate lined diffuser which discharges into the drying tower. HF product is withdrawn from the top of this tower.

The economics and cost of the process show that RHT process can be compared favourably with fluorspar plants. The corrosion rate in higher temperature sections of the plant is quite low with consequent reduction in the alloy required.

[*Chem. Age Internat*, 106 (2813) (1973), 9]

Organic Versus Chemical Farming

Ir. H. Vander Molen of the Central Stikstoff of Verkoopkantoor NV(CSV) of the Netherlands in a paper published in the journal Stikstoff discussed the arguments against the use of chemical fertilizers by the proponents of organic farming in particular nitrogen and for the most part effectively countered.

The four main points on the bad effects of chemical fertilizer made by organic farmers are : (1) that artificial nitrogen used in large quantities leads to a deterioration of protein quality ; (2) that over-supply of nitrogen seriously disrupts the mineral balance in plants ; (3) that plants and animals are forced by modern agricultural methods and are thus adversely affected as to quality and are less healthy than those raised by using organic manures ; and (4) that a great deal of the enrichment of surface water (eutrophication) with nitrogen and phosphate is claimed to be caused to a considerable extent by agricultural effluents and run off fertilizer nutrients from farm land.

Considering the above points, the use of large quantities of nitrogenous chemical fertilizers is supposed by organic farmers to result in a deterioration in the quality of protein and results in a reduction in the content of essential amino acids and the storage of simpler nitrogen compounds such as nitrates in the plant tissue. This state of affairs is alleged to be a burden on the metabolism of animals.

The use of large quantities of nitrogen on grass does not appear to upset the balance of minerals in the plant, as the higher the application rate the higher the content of both nitrogen and other minerals in the grass.

During the 1960's special nitrogen experimental farms were set up in the Netherlands to test the consequences of very high levels of N-fertilization on the health of animals and crops. Over all, during the 3 years period milk production per cow on these nitrogen experimental farms averaged 250 kg more than the country-wide average was 2.5% at an average N usage of 150 kg/ha.

By taking appropriate precautions no occurrences of nitrate poisoning in cattle were experienced on the experimental farms. Comparisons were made between groups of cows fed from land given 500 kg and 150 kg N respectively. Milk per lactation period, milk yield per day, butter fat %, percentage in calf after one

insemination for cows fed in the farm with 500 kg. N/ha. were found to have given better results than cows fed on 150 kg. N/ha.

In a recent paper in Stikstoff (No. 15/1972,) a comparison was made by Ir. G. J. Kolenbrander of the eutrophication of surface water caused by agriculture and the urban population. It was found that 4% of the nitrogen applied as fertilizers leached out from farmland soil as a whole. The rate of leaching from arable land was just over 13% of the nitrogen applied, but in the case of grassland only 1% of the fertilizer was found in surface water supplies. The author states that nitrogen reaches rivers not only from agriculture but through industrial effluent and sewerage as well and that contribution of fertilizers to eutrophication is nearly negligible. He also states that with phosphates a total of only 0.6 kg/ha leaches annually from agricultural land, whereas the contribution from household was carried away through the sewerage system amounts to about 16 kg/ha or 25 times as much as from farmland.

The Dutch author concludes his article by saying that the use of organic fertilizers could hardly increase total food production because organic manuring only means the transfer of fertility from one place to another, whereas the use of chemical fertilizers introduces nutrients which have not previously been circulated in agriculture. Without this additional supply of nutrients the world population could not be fed.

In the current situation where it is expensive and often uneconomic to apply organic manures, much of the organic material and its contained nutrients are wasted, being no longer circulated in the crop growing system. If every practicable use of organic manures were made, the rate of depletion of the available world reserve of fertilizer nutrients could be slowed down. In China organic forms of fertilizer are very widely used and little is wasted and it has been calculated that these manures contributed approximately the same quantity of nutrients as are provided by chemical fertilizers which is over 40 kg./ha. The average nutrient application to crops in China exceeds 80 kg./ha which is well above the level of most other countries in Asia except Japan, South Korea and Taiwan. If other countries were to follow China's example, the rate of

depletion of the world's chemical fertilizer reserves would be appreciably reduced.

[*Nitrogen*, No. 86 Nov. Dec. 1973, 29]

Heavy Water Integrated with Ammonia Plant

Heavy water is a vital material in the production of atomic energy. Nuclear power station using natural uranium as fuel requires heavy water as moderator. At present Canada is the largest producer of heavy water. India is the second country committed for production of heavy water. The Tarapur nuclear power station is based on the utilization of enriched uranium and ordinary water, whereas the Ranapratapsagar (200 MW Capacity) and Kalpakam (400 MW) power stations are based on natural uranium and heavy water. About 0.7-1 te of heavy water is required as an inventory material for every megawatt of power capacity. Though heavy water is not consumed during the reaction, the losses (3-10%) have to be made up.

The only heavy water plant in India is in the Nangal fertilizer factory (FCI) having an annual capacity of 14 tes. The Atomic Energy Commission have made plans for a 100 t/yr plant at Ranapratapsagar, a 67.2 t/yr plant at GSFC Baroda, 72 te plant Tuticorin and 60 te plant at Talcher. The Nangal plant employs hydrogen distillation with pre-enrichment by electrolysis.

The heavy water plant in the Gujarat State Fertilizer Co. Baroda will be based on Menothermic $\text{NH}_3\text{-H}_2$ Isotopic Exchange Process offered by the consortium of FFM Sulzer and Air Liquide, known as GELPRA. Theoretically, about 1 t/yr of heavy water can be produced for every 10 t/day of ammonia production. With the existing two ammonia plants having total capacity of 950 tons of NH_3 /day and the third synthesis gas project (100 t/d), it is possible theoretically to get 105 tons/yr of heavy water. However, in actual practice the production will be 67.2 t/yr. because (i) the efficiency of deuterium ex-

traction in heavy water plant is around 84%, (ii) shift exchange of deuterium in ICI Steam Naphtha reforming process, (iii) leakage etc. in the heavy water plant.

The synthesis gas at about the discharge pressure of hypercompressors (640-650 Kg/ cm^2G) and 400°C will be used as feed source of deuterium. The average composition of synthesis gas is H 74.2% N 24.5% CH_4 0.75%, A 0.3%, $\text{CO} + \text{CO}_2$ 1.0 ppm; Deuterium 125 ppm. The synthesis gas contains around 10 ppm carbon oxides, moisture, oil and traces of some impurities. With the coming up of ultramethanators, the carbon oxide is likely to go down to 1 ppm. The heavy water plant has incorporated charcoal absorption tower alumina driers and purifiers to remove oil, moisture and the traces of carbon oxides. If the carbon oxides are present in syn. gas, they react with the potassium amide used as a catalyst, resulting in the clogging of trays of the isotopic exchange tower.

Deuterium extraction takes place in the isotopic exchange tower (IET) consisting of 11 ejector type trays wherein the syn. gas and liq. $\text{NH}_3 + \text{KNH}_2$ catalyst 50% are brought in intimate contact. Each tray consists of 84×3 nos. of ejectors and draws out liquid NH_3 as it passes through the ejectors. Each plate is equipped with an efficient separation system and two hermetically sealed pumps to transport liquid NH_3 to the lower tray. The syn. gas from the top of IET may contain upto 12.5 ppm of deuterium (D_{20}). The enriched stream deuterium concentration is around 4.5 N(IN = 125 ppm). Liquid NH_3 required as a reflux in heavy water plant will be made in the secondary NH_3 synthesis unit (300 t/d) to be set up in heavy water plant area. The operating conditions in IET are -20°C and 625-650 kg./ cm^2G .

The reaction enrichment $\text{NH}_3(1) + \text{HD(g)} \rightleftharpoons \text{NH}_2\text{D(1)} + \text{H}_2$ is carried out in a tower similar to IET at 20°C and 140 kg./ cm^2g . The deuterium concentration goes upto 204N by contact with enriched cracked gases from NH_3 crackers. The

depleted cracked gases from the top of the enrichment tower are compressed in cracked gas compressor and joins the main syn. gas stream from GSFC at the inlet of the IET. The catalyst recovery is done by passing the enriched stream of liq. $\text{NH}_3 + \text{KNH}_2$ catalyst through distillation columns. Cracking of the enriched NH_3 is done in an NH_3 cracker operating at about $400\text{-}500^\circ\text{C}$ and 145 kg./ cm^2 . The gaseous mixture contains H_2 , N_2 and D_2 . A part of the stream is taken to the finishing section while the remaining stream goes to the enrichment tower. Finishing section yields a highly concentrated deuterium which is oxidized by supplying hot air. Nitrogen etc. are separated and heavy water is collected.

The special features of the heavy water plant integrated with GSFC's ammonia plants are: (i) The synthesis gas has deuterium concentration around 110 ppm. In the reforming process, in which steam is added, deuterium in hydrogen gets transferred to the steam and then to the steam condensate and shift conversion also promotes this transfer. To avoid this depletion, the condensate obtained before the CO_2 absorption stage can be recycled back after treating this contaminated condensate. Condensate recycling will also help in reducing the amount of effluent and saving in condensate water; (ii) synthesis gas compressors of the Ammonia I and II plants will compensate for the additional expected pressure drop estimated at around 37 kg./ cm^2 . The major drop occurs in the isotopic exchange tower of the heavy water plant; (iii) the ultra pure syn. gas returning from heavy water plant will help to increase the production capacity of the existing ammonia synthesis units and production at increased rate can be achieved if additional syn. gas is available; (iv) in order to meet the operation emergencies of heavy water plant an auto by-pass loop of the syn. gas lines is provided at the heavy water plant so as not to disturb the operations of ammonia synthesis units of GSFC.

[*GSFC Trg. Bull.*, 8 (1) (1974), 27]

CFRI's Pilot Plant on Coal-Based Fertilizers

The dream of coal-based fertilizer is a step nearer to reality now that the Central Fuel Research Institute at Dhanbad has embarked on a Rs. 1 lakh pilot plot for the commercial production of coal-based fertilizers. ICAR is evaluating the process developed by CFRI. In this process coal is oxidized to produce a water-soluble polycarboxylic acid having a yield of 70 to 80 per cent. This acid is then converted into ammonia polycarboxylate, a unique ammonia fertilizer proved to be as good as traditional fertilizers. A preliminary cost estimate reveals that production of 1 kg. of this new *carbonaceous* fertilizer based on the present state of development may not exceed 80 paise. Carbonaceous fertilizer is receiving vast acceptance around the world. Japan, for instance had developed a process for producing ammonium nitro humate from lignite. However, the CFRI scientists claim that the Indian product is radically different from the Japanese one and the availability of nitrogen in the Japanese product is about half that in the coal-based fertilizers developed by Indian scientists. Coal-based fertilizers in fact have an edge over the traditional fertilizers, the continuous use of which will make the soil depleted of its natural humus content. The fertility of the soil goes down unless corrective measures are taken through application of compost fertilizers. But coal-based fertilizers provide an ideal substitute for such super-chemical fertilizers and here lies its importance. Our government has recognized the inevitability of coal-based fertilizers and a lot of schemes are, therefore, underway to implement various projects in this regard. The CFRI plans will definitely give a shot in arm to India's efforts to bridge the gap between the demand and supply of fertilizers.

[CEW, 9 (9) (1974), 49]

Combined Gas and Steam-turbine Process

Power economists are turning their attention towards new technologies in particular, for converting coal into electricity since nuclear power stations take longer time to build and nuclear development is very costly. Further, many countries still have large deposits of bituminous coal.

A 170-MW KDV Kellermann power plant has been installed at Luenen based on the new process—the STEAG-combined gas/steam turbine cycle process with Lurgi

pressure gasification system. Such a plant will have the following advantages: (a) It will reduce the total emission of noxious matter by about 75 per cent. Emission of dust and fluorine will be almost completely prevented, reducing SO_2 emission by 90 per cent and NO_x emission probably by 50 per cent; (b) the thermal efficiency will also increase from 39 to 43%; (c) a 15 per cent reduction in investment costs can be expected mainly because of the cost-saving construction of combined gas/steam turbine processes with the pressurized boiler.

Process: The coal is fed to the gasifier, where the gasifying media are steam and air. It is gasified under a pressure of 280 psig. The flue gas leaves the gasifier at 550°C and passes to the scrubber to be cleaned there from tar and dust. A H_2S separating plant is likely to be installed at this point in the flow. The clean gas is expanded from the 280 psig pressure level in an expansion turbine and then burned in the pressurized boiler with a portion of gas-turbine air. The exhaust gases leave this boiler at 820°C and are expanded by means of a gas turbine. The capacity of the gas turbine is 74 MW maximum. The exhaust gases from the turbine are passed at 400°C to a waste-heat boiler to 330°C. The exhaust gases leave the stack at 160°C.

The steam generated in the pressurized boiler is passed to steam turbine at 520°C and 1800 psig. The electrical rating of the steam turbine is 96 MW.

[CEER, 6 (6) (1974), 23]

R and D Management

In delivering the keynote address, at the seminar of the Directors of CSIR laboratories on the concepts and techniques of R and D management held at Hyderabad from July 31 to Aug. 3, 1974, Dr. Y. Nayudamma, Director General CSIR, stressed the need for scientific management of R and D in the national laboratories as the subject has assumed importance in recent years because R and D involved much more funds than in the past. He emphasised the role of the directors of laboratories as research managers. He outlined the peculiarities of CSIR and the difficulties it faced, viz. (i) it did not have a captive market; (ii) it handled diverse areas of research; and (iii) market economy did not operate either for scientific manpower or for the results of their research. Instructions have been issued

to the effect that project planning, budgeting and monitoring be introduced in all the national laboratories by 1975. Discussions on the inaugural address were mainly confined to the role of NCST in transforming the needs of the people into research programmes and in tying up research programmes with national plans. Further deliberations of the seminar were focussed on the following 4 topics: (i) setting of objectives, (ii) organization structure and dynamics, (iii) project management and (iv) human resources management.

Objectives: The objectives, as presently defined by various laboratories, could be considered as charters. These could be set at different levels of an organization and would change as the external or internal environment changed. The objectives provided guidelines and basis for the appraisal of the organization and of individuals at different levels in the organization. Actually all other management functions stem from the objectives, i.e. (i) a suitable organization structure is adopted to achieve the objectives; (ii) it provides basis for planning and control of various activities; (iii) participation in the setting of objectives can be the most important motivating factor for managers, scientists and technologists.

Organization Structure & Dynamics: The organization structure of a research laboratory depended on the activities it performed, e.g. basic, applied or developmental research. Four kinds of structures were proposed, viz. broad-span, functional or disciplinary, project, and combination of the above. A flat type of structure with fewer levels would depend upon the management style of the director and should match the objectives and needs. Delegation of authority—formal or informal—also depended on the structure.

Project Management: This had three aspects, viz. project selection and planning project monitoring and control, and marketing of results of research. For project selection and for allocation of priorities, the following two general criteria could be used: (i) growth in GNP and (ii) equitable distribution of national income. Project selection could be considered as an investment decision and economic cost-benefit analysis could be successfully used for project evaluation and selection. The concept of opportunity cost could also be utilized to assess the comparative benefits of current or future projects.

Considerable stress was laid on the use of exploratory research, literature survey and preparation of detailed project plans. This would involve articulation, decomposing and phasing of the various activities of a research project.

The discussion on marketing of research was mainly concerned with the centralization of this activity in the National Research Development Corpr. of India,

as against its decentralization in individual laboratories. The consensus was that some degree of decentralization was necessary.

Management of Human Resources : As selection, training, evaluation, promotion and motivation of scientific workers are an important management function, most of the discussion centred round evaluation and promotion procedures. Self-evaluation as well as evaluation by colleagues,

both lower and higher in rank than the person to be evaluated, were suggested as an alternative to the present methods. Bureaucratic procedures and the status system in the laboratories were major disincentives for scientists. Leadership style is the most important variable in the effective management of human resources at laboratory level.

[*CSIR News*, 24 (18) (1974), 137]

STATISTICS

TABLE 1—TOTAL RESERVES OF COAL AND LIGNITES IN INDIA, mil. tes

Field (1)	Class I (2)	Class II (3)	Class III (4)	Class IV (5)	Unclassi- fied (6)	Total (7)	Ind. (8)	Inf. (9)	G. Total (10)
West Bengal									
(1) Raniganj (A small portion falls in Bihar)									
(a) Medium coking	89.72	87.25	12.48	—	198.62	388.07	296.73	200.85	885.65
(b) Semi-coking	164.04	48.32	3.46	—	87.25	303.07	304.42	193.10	800.59
(c) Weakly coking	134.54	87.96	—	—	53.15	275.65	173.97	344.41	794.03
Total	388.30	223.53	15.94	—	339.02	966.79	775.12	738.36	2480.27
(d) Non-coking	24.61	1418.76	26.77	4.86	1328.65	3059.65	5192.03	8832.29	17084.87
Total	412.91	1642.29	298.71	4.86	1667.67	4026.44	5968.05	9570.65	19565.14
(2) Bansjora non-coking	—	—	11.92	—	—	11.92	26.84	—	38.76
(3) Dasjeeling non-coking	—	—	—	—	—	—	—	15.00	15.00
Bihar									
(4) Jharia									
(a) Prime coking	976.77	2176.77	226.43	0.39	264.05	3644.41	1535.71	460.73	5640.85
(b) Medium coking Low volatile	4.18	117.19	355.65	—	532.07	1009.09	562.11	364.15	1935.35
(c) Medium coking Medium volatile	33.02	5.53	3.69	2.34	19.78	64.36	119.13	—	183.49
Total	1013.97	2299.49	585.77	2.73	815.90	4717.86	2216.95	824.88	7759.69
(d) Non-coking	3.87	37.20	213.94	67.28	7307	395.36	1131.46	3530.90	5057.72
Total	107.84	2336.69	799.71	70.01	888.97	5113.22	3348.41	4355.78	12817.41
(5) East Bokaro									
Medium coking	33.58	701.80	382.61	338.64	6.09	1462.72	435.75	94.48	1992.95
(6) West Bokaro									
(a) Medium coking	23.30	40.86	136.07	—	36.87	237.10	325.50	40.71	603.31
(b) Semi to weakly coking	—	82.28	481.28	4.64	66.98	635.18	1767.65	317.24	2720.07
Total	23.30	123.14	617.35	4.64	103.85	872.28	2093.15	357.95	3323.38
(7) Ramgarh									
(a) Medium coking	—	100.48	94.03	—	—	194.51	16.23	16.43	227.17
(b) Semi to weakly coking	0.27	72.42	215.04	—	16.67	304.40	344.54	60.04	708.98
Total	0.27	172.90	309.07	—	16.67	498.91	360.77	76.47	936.15
(8) Giridih									
(a) Prime coking	—	8.80	—	—	—	8.80	1.55	—	10.35
(b) Medium coking	—	—	4.72	20.44	—	25.16	1.77	—	26.93
Total	—	8.80	4.72	20.44	—	33.96	3.32	—	37.28
(9) North Karanpura									
(a) Medium coking (high ash)	0.51	42.27	234.00	21.39	102.65	400.82	2359.52	555.56	3315.90
(b) Non-coking	8.58	248.47	284.76	16.37	41.11	599.29	4742.43	11.12	5352.84
Total	9.09	290.74	518.76	37.76	143.76	1000.11	7101.95	566.68	8668.74
(10) South Karanpura									
Non-coking	13.11	523.25	562.67	69.90	394.66	1563.59	2154.97	728.15	4446.71
(11) Auranga									
Non-coking	—	—	—	—	—	—	—	118.64	118.64
(12) Hatar									
Non-coking	—	—	—	—	—	—	—	80.75	80.75
(13) Daltonganj									
Non-coking	0.34	3.70	1.13	—	0.27	5.44	82.47	—	87.91
(14) Deogarh									
Non-coking	1.02	1.47	7.36	—	1.80	11.65	20.34	6.31	38.30
(15) Rakmohal									
Non-coking	—	1.32	14.82	12.26	—	28.40	517.10	2136.47	2681.97

TABLE 1—TOTAL RESERVES OF COAL AND LIGNITES IN INDIA, mil. tes—Contd.

Field (1)	Class I (2)	Class II (3)	Class III (4)	Class IV (5)	Unclassi- fied (6)	Total (7)	Ind. (8)	Inf. (9)	G. Total (10)
Madhya Pradesh									
(16) <i>Pench-Kanhan-Tawa Valley</i>									
(a) Medium coking (in Damua & Tandsi area)	—	69.45	—	—	—	69.45	193.30	—	262.75
(b) Non-coking	33.99	68.14	72.77	—	17.90	192.80	9.04	—	201.84
Total	33.99	137.59	72.77	—	17.90	262.25	202.34	—	464.59
(17) <i>Tawa Valley</i> (Gurganda area)									
Non-coking	—	—	4.60	—	—	4.60	114.70	—	119.30
(18) <i>Pathakhera</i>									
Non-coking	—	—	26.33	87.26	—	113.59	—	—	113.59
(19) <i>Sonhat</i>									
(a) Semi-coking (in Churcha area)	30.58	5.59	—	—	—	36.17	10.40	—	46.57
(b) Non-coking	55.82	5.05	24.37	33.42	—	118.66	162.87	—	281.53
Total	86.40	10.64	24.37	33.42	—	154.83	173.27	—	328.10
(20) <i>Umaria</i>									
Non-coking	—	—	12.35	—	—	12.35	—	31.97	44.32
(21) <i>Korar</i>									
Non-coking	—	—	—	—	—	—	—	2.96	2.96
(22) <i>Sendurgarh</i>									
Non-coking	—	—	—	—	—	—	—	40.60	40.60
(23) <i>Haslo-Arand</i>									
Non-coking	—	—	—	—	—	—	—	1742.30	1742.30
(24) <i>Mand-Raigarh</i>									
Non-coking	—	—	1.15	—	—	1.15	1.32	974.60	977.07
(25) <i>Jehilla</i>									
Non-coking	—	6.43	33.00	—	—	39.43	—	29.00	68.45
(26) <i>Bisrampur</i>									
Non-coking	55.88	80.69	5.50	—	1.62	142.69	229.26	—	371.95
(27) <i>Jhagrakhand</i>									
Non-coking	—	—	—	—	—	—	26.50	—	26.50
(28) <i>Jhlimili</i>									
Non-coking	0.23	14.56	—	3.09	0.71	18.59	62.63	—	81.22
(29) <i>Chirimiri</i>									
Non-coking	72.42	167.72	19.95	—	1.87	262.01	51.80	14.30	328.11
(30) <i>Korba</i>									
Non-coking	29.05	168.75	114.15	94.19	—	406.14	452.68	—	858.82
(31) <i>Sohagpur</i>									
Non-coking	12.19	67.74	12.09	—	0.73	92.75	407.03	26.00	525.78
(32) <i>Lakhanpur</i>									
Non-coking	0.71	4.85	1.29	—	4.07	10.92	175.43	80.00	266.35
(33) <i>Mohpani</i>									
Non-coking	—	0.44	0.62	0.17	—	1.23	—	—	1.23
(34) <i>Singrauli (Part in U.P.)</i>									
Non-coking	—	—	2184.27	539.75	—	2724.02	2170.53	4226.67	9121.22
Orissa									
(35) <i>Talcher</i>									
Non-coking	9.25	122.19	286.26	441.12	2.84	861.66	2381.82	—	3243.48
(36) <i>Ib-River</i>									
Non-coking	—	5.18	—	—	28.56	33.74	29.14	1810.12	1873.00
Maharashtra									
(37) <i>Chanda-Wardha</i>									
Non-coking	—	46.26	150.93	4.16	15.90	217.25	499.24	1315.51	2032.00
(38) <i>Umrer</i>									
Non-coking	—	42.10	42.93	—	—	85.03	10.13	—	95.16
(39) <i>Kamptee</i>									
Non-coking	—	56.27	119.31	—	—	175.58	200.31	28.55	404.44
(40) <i>Bander</i>									
Non-coking	—	—	—	—	—	—	90.05	—	90.05

TABLE 1—TOTAL RESERVES OF COAL AND LIGNITES IN INDIA, mil. tes—*Contd.*

Field (1)	Class I (2)	Class II (3)	Class III (4)	Class IV (5)	Unclassi- fied (6)	Total (7)	Ind. (8)	Inf. (9)	G. Total (10)
Andhra Pradesh									
(41) <i>Godavari Valley Non-coking</i>	—	557.90	407.24	0.68	12.13	977.95	1077.18	—	2055.13
Grand total for Gondwana Fields	1810.63	7295.41	7047.94	1762.35	3310.07	21,226.40	30,468.48	28,429.91	80,124.79
Tertiary Coalfields Assam, Meghalay, Arunachal and Nagaland									
(42) <i>Namchik-Namphuk</i>	9.00	—	—	—	—	9.00	82.00	—	91.00
(43) <i>Garo Hills</i>	127.00	—	—	—	—	127.00	—	295.00	422.00
(44) <i>Langrin</i>	—	—	—	—	—	—	—	81.00	81.00
(45) <i>Cherrapunji and others</i>	—	—	—	—	—	—	—	9.50	9.50
(46) <i>Makum</i>	—	—	—	—	—	—	191.00	—	191.00
(47) <i>Nazira</i>	—	—	—	—	—	—	—	10.00	10.00
(48) <i>Jhanzi-Disai Valley</i>	—	—	—	—	—	—	—	2.50	2.50
(49) <i>Delli-Jeypore</i>	—	—	—	—	3.00	3.00	17.00	—	20.00
(50) <i>Koilajan</i>	—	—	—	—	—	—	0.60	—	0.60
Total for Tertiary coalfields*	136.00	—	—	—	3.00	139.00	290.60	398.00	827.60
Grand Total (coking and non-coking)	1946.63	7295.41	7047.94	1762.35	3313.07	21,365.40	30,759.08	28,827.91	80,952.39

*Proved reserves for Namchik-Namphuk and Garo Hills coalfields taken under class I category.

Note—The classification is based on Indian Standard Procedure which is as follows.

Field	Lignite Reserves (M. Tonnes)			
	Proved	Indi- cated	In- ferred	Grand total
(1) Neyveli	1717	202	—	1919
(2) Umarsar	10.70	—	—	10.70
(3) Matanomadh & Lefri	33.86	—	—	33.86
(4) Panandhro	—	—	—	—
(5) Akhrimota	33.00	—	—	33.00
(6) Nichahom	—	—	8.4	8.4
(7) Palana	—	—	20.3	20.3

For low moisture coals	
Class I	Ash not exceeding 17%
Class II	Ash exceeding 17% but not exceeding 24%
Class III	Ash exceeding 24% but not exceeding 35%
Class IV	Ash exceeding 35% but not exceeding 50%
For high moisture coals	
Class I	Ash+moisture not exceeding 19%
Class II	Ash+moisture exceeding 19% but not exceeding 28%
Class III	Ash+moisture exceeding 28% but not exceeding 40%
Class IV	Ash+moisture exceeding 40% but not exceeding 55%

[FRI News, 23 (1973), 48]

N.B.—Reserves have been calculated for seams 1.2 m and above in thickness and generally up to a depth of 609 m except in Jharia, where, reserves have been taken up to a depth of 913 m in certain sectors. In Jharia reserves have been calculated by and large up to the depth limits, where the seams have retained their prime coking characteristics.

TABLE 2—INDUSTRYWISE CONSUMPTION OF COAL AND LIGNITE IN INDIA

Consuming Sector	(Million Tonnes)	
	1969-70	1970-71
1. Railways (Loco)	16.61	15.34
2. Steel Plants:		
(a) Coking coal	13.71	12.74
(b) Blendable coal	0.76	0.79
3. Merchant Coke Ovens:		
(a) Coking coal	2.40	2.17
(b) Blendable coal	0.10	0.07
4. Thermal Power Plants	10.24	10.80
5. Cement Plants	3.64	3.52
6. Textiles (cotton)	1.70	1.55
7. Paper & Paper Board	0.90	1.01
8. Brick Burning	4.78	3.11
9. Domestic Coke	3.64	3.24
10. Export	0.35	0.46
11. Others Including Collieries' Own Consumption	16.25	15.19
Grand Total:	74.59	69.99

[FRI NEWS, 23 (1973), 53]

TABLE 3—EX-FACTORY PRICE OF SINGLE SUPERPHOSPHATE IN INDIA (MINIMUM 16% W.S. P_2O_5)
(Effective from June 1, 1974)
(Bulk & bagged)

Name of Factory	For Material Packed in 100 kg. packing		
	B-Twill Polythene-lined Jute Bags	HDPE woven sacks	Bulk (without packing)
<i>North</i>			
(Rupees per metric tonne)			
1. D.C.M. Chemicals, Delhi	754	768	693
2. Hindustan Zinc Ltd., Udaipur	690	704	629
3. Ralli Chemicals Ltd., Magarwara	740	754	679
<i>West</i>			
1. Adarsh Chemicals & Fertilizers Ltd., Udhna	721	735	660
2. Paushak Ltd., Baroda	721	735	660
3. Anil Starch Products Ltd., Bhavnagar	690	704	629
4. Bharat Fertilizers Industries, Bombay	690	704	629
5. Dharamsi Morarji Chemical Co., Kumhari	714	728	653
6. Dharamsi Morarji Chemical Co., Ambernath	696	710	635
7. J. K. Chemicals Ltd., Bombay	690	704	629
8. Western Chemicals Industries, Bombay	690	704	629
9. West India Chemicals, Loni-Kalbhere	719	733	658
10. Anish Chemicals Ltd., Ahmedabad	720	734	659
<i>East</i>			
1. Bihar State Superphosphate Factory, Sindri	732	746	671
2. Jayshree Chemicals & Fertilizers, Khardah	690	704	629
3. Phosphate Co. Ltd., Rishra	690	704	629
<i>South</i>			
1. Andhra Fertilizers Ltd., Tadepalli	723	737	662
2. Coimbatore Pioneer Fertilizers Ltd., Coimbatore	721	735	660
3. E.I.D.—Parry Ltd., Ranipet	690	704	629
4. F.A.C.I. Alwaye	690	704	629
5. Hyderabad Chemicals & Fertilizers Ltd., Maula Ali	725	739	664
6. Kothari (Madras) Ltd., Ennore	690	704	629
7. Krishna Industrial Corp., Nidadavole	710	724	649
8. Shaw Wallace & Co. Ltd., Avadi	690	704	629
9. Andhra Sugars Ltd., Tanuku	710	715	640

Note:—1. The manufacturers may charge of Rs. 12.00 (Rupees twelve only) extra per tonne for the material packed either in B-Twill polythene lined jute bags or HDPE woven sacks of 50 kg. capacity.
2. Manufacturers may charge of Rs. 60.00 (Rupees sixty only) extra per tonne for granulated superphosphate.
3. These prices are exclusive of excise duty and other local taxes.

[Fert. News 19(6) (1974)]

TABLE 4—RECOVERABLE AND TOTAL ESTIMATED ENERGY RESERVES IN THE USA

Energy Fuel	Known or proved Recoverable Reserve			Estimated Reserves-in-Place		
	Known Reserved	Quadril-lion Btu*	Per cent of Total Btu*	Estimated in-Place	Quadril-lion Btu*	Per cent of Total Btu*
Coal, billion tons	390.0	8,190	88	1,605	33,000	68
Petroleum, billion bbl	38.1	214	2	430	2,400	5
Natural gas, trillion ft ³	278.8	287	3	2,380	2,500	5
Natural gas liquids, billion bbl	7.3	29	neg.	70	280	1
Oil in bituminous rocks, billion bbl	1.3	7	neg.	5	30	neg.
Shale oil, billion bbl	80.00	450	5	1,600	9,000	19
Uranium oxide (U ₃ O ₈), thousand tons**	300.0	135	2	2,400	1,080	2
		9,312	100		48,240	100

* Reserves converted to Btu according to the following heat values: Coal, 21,000,000 Btu/ton; petroleum, oil from bituminous rock, and oil shale, 5,623,000 Btu/bbl; natural gas liquids, 4,011,000 Btu/bbl; natural gas, 1,031 Btu/ft³; and uranium oxide, 450 million Btu/ton (compared on basis of use in light-water reactors with plutonium recycle).

** Uranium reserves relative \$ 10/lb and \$ 32.50/lb U₃O₈ in proved and estimated categories, respectively.

Source:—National Coal Assn. compiled from government and private sources; revised by Chemical Engineering.

[Chem. Engng, 81 (7) (1974), 30]

TABLE 5—PLANT FOOD CONSUMPTION OF AGRICULTURAL LAND IN INDIA

Zone/State	Consumption, kg hectare of agricultural land*							
	1972-73				1973-74			
	N	P ₂ O ₅	K ₂ O	Total	N	P ₂ O ₅	K ₂ O	Total
South	13.41	5.88	3.87	23.11	13.42	5.89	3.84	23.15
Andhra Pradesh	12.23	4.90	1.66	18.79	11.77	5.30	1.40	18.67
Kerala	10.84	7.31	6.27	24.42	11.88	7.72	7.34	26.94
Karnataka	8.39	4.38	3.08	15.85	8.35	3.77	3.08	15.20
Tamil Nadu	24.66	9.18	8.33	42.17	25.12	9.18	8.16	42.46
Pondicherry	64.58	37.50	21.61	123.69	57.96	31.67	22.78	112.41
West	7.08	2.85	1.83	11.76	8.58	3.96	1.30	13.84
Gujarat	10.14	4.80	0.95	15.89	12.51	5.45	1.15	19.11
Maharashtra	5.44	1.79	2.30	9.53	6.45	3.12	1.35	10.92
Goa	8.60	6.11	2.60	17.31	13.48	9.00	4.82	27.30
Dadra, Nagar Haveli	N.A.	N.A.	N.A.	N.A.	20.40	12.00	5.20	37.60
Central	8.08	2.26	0.95	11.29	6.53	1.82	0.71	9.06
Madhya Pradesh	3.90	1.65	0.35	5.90	3.23	1.77	0.30	5.30
Uttar Pradesh	15.68	4.11	2.06	21.85	12.30	2.74	1.47	16.51
Rajasthan	2.97	0.41	0.21	3.59	3.09	0.64	0.24	3.97
Delhi	18.39	4.78	1.15	24.32	18.56	3.98	1.10	23.64
North	24.00	5.88	1.65	31.62	28.06	7.46	2.07	37.59
Haryana	16.62	1.64	0.52	18.78	17.99	2.89	0.79	21.76
Himachal Pradesh	2.28	0.84	0.52	3.64	1.66	0.54	0.32	2.52
Jammu & Kashmir	7.30	1.54	0.59	9.43	9.77	2.64	1.03	13.44
Punjab	42.71	12.57	3.33	58.61	50.29	14.95	4.04	69.28
East	5.85	*1.46	0.29	18.60	5.23	1.52	1.32	8.07
Assam	2.06	0.53	0.59	3.18	0.66	0.11	0.43	1.20
Bihar	7.80	1.65	0.95	10.40	5.98	1.60	0.61	8.19
Orissa	4.25	1.05	0.61	5.91	4.54	1.25	0.78	6.57
West Bengal	9.71	2.23	3.16	15.10	7.01	2.39	3.49	12.89
Manipur	5.44	1.17	0.33	6.94	6.98	1.18	0.57	8.73
Tripura	2.22	1.09	0.32	3.63	2.41	0.62	0.65	3.68
Nagaland	N.A.	N.A.	N.A.	N.A.	0.49	0.29	0.29	1.07
Meghalaya	N.A.	N.A.	N.A.	N.A.	0.78	0.30	0.17	1.25
All-India	9.85	3.25	1.84	14.94	9.93	3.43	1.70	15.06

Note:—These figures are based on consumption data furnished at the Zonal Conferences of Fertilisers, Ministry of Agriculture, New Delhi, N.A. Not available.

* It includes total cropped area, permanent pasture other grazing lands and land under miscellaneous tree crops, groves, etc.

[Fert. News, 19 (5) (1974), 34]

TABLE 6—NET AVAILABILITY OF CEREALS AND PULSES IN INDIA

Year	Popula- tion (million)	Cereals (Million tonnes)				Pulses Net avail- ability, Mil. tonnes	Per capita net availability per day					
		Net pro- duction	Net imports	Change in Govt. Stock	Net avail- ability		Cereals	Pulses	Total	Cereals	Pulses	Total
(In ounces)			(In grams)									
1956	397.3	50.43	1.39	—0.60	52.42	10.23	12.72	2.48	15.20	360.5	70.5	430.9
1961	442.4	60.89	3.49	—0.17	64.55	11.14	14.10	2.43	16.53	399.7	69.0	468.7
1962	452.2	61.85	3.64	—0.36	65.85	10.24	14.07	2.19	16.26	399.0	62.0	461.0
1963	462.0	60.19	4.55	—0.02	64.76	10.08	13.54	3.11	15.65	384.0	59.8	443.8
1964	472.1	61.79	6.26	—1.24	69.29	8.81	14.14	1.80	15.94	401.0	51.0	452.0
1965	482.5	67.33	7.45	+1.06	73.72	10.85	14.77	2.17	16.94	418.6	61.6	480.2
1966	493.2	54.60	10.34	+0.14	64.80	8.68	12.70	1.70	14.40	360.0	48.2	408.2
1967*	504.2	57.65	8.66	—0.26	66.57	7.30	12.76	1.40	14.16	361.7	39.7	401.4
1968*	515.4	72.58	5.69	+2.04	76.23	10.57	14.25	1.98	16.23	404.1	56.0	460.1
1969*	527.0	73.14	3.85	+0.46	76.53	9.09	14.04	1.67	15.71	397.9	47.0	445.2
1970*	538.9	76.83	3.58	+1.11	79.30	10.20	14.22	1.83	16.05	403.2	51.9	455.1
1971*	550.8	84.53	2.03	+2.57	83.99	10.32	14.74	1.81	16.55	417.8	51.3	469.1
1972*	562.5	82.31	—0.48	—4.70	86.53	9.70	14.83	1.66	16.49	420.3	47.1	467.4
1973*	574.2	75.00	3.60**	—0.66	79.26	8.30+	13.34	1.40	14.74	378.2	39.6	417.8

* Provisional + Relates to net production only ++ Gross imports.

Note:—Net production has been taken as 87.5 per cent of the gross production 12.5 percent being provided for feed, seed requirements and wastage.

[Records & Statistics, Quart. Bull. of Eastern Econ., 25 (2) (1974), 81]

TABLE 7—NET AVAILABILITY, PROCUREMENT AND PUBLIC DISTRIBUTION OF FOODGRAINS IN INDIA (Million tonnes)

Year	Net Production of Foodgrains	Imports	Net Availability of Foodgrains	Procurement	Public Distribution	Col. 3 as % of Col. 4	Col. 5 as % of Col. 2	Col. 6 as % of Col. 4
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1956	60.67	1.44	62.66	0.04	2.08	2.8	0.1	3.3
1965	78.20	7.46	84.59	4.03	10.08	8.8	5.2	11.9
1966	63.30	10.36	73.50	4.01	14.09	14.1	6.3	19.2
1967(P)	64.95	8.67	73.87	4.46	13.17	11.7	6.9	17.8
1968(P)	83.17	5.69	86.82	6.81	10.22	6.6	8.2	11.8
1969(P)	82.26	3.87	85.65	6.38	9.39	4.5	7.8	11.0
1970(P)	87.06	3.63	89.52	6.71	8.84	4.1	7.7	9.9
1971(P)	94.87	2.05	94.33	8.86	7.83	2.2	9.3	8.3
1972(P)	92.02	0.45	96.24	7.70	10.48*	0.5	8.4	10.9
1973(P)	83.30	3.60	87.56	8.43	11.50	4.1	10.1	13.1

(P) Provisional *Excludes exports to Bangladesh

[Records & Statistics, Quart. Bull. of Eastern Econ., 25(2) (1974), 81]

TABLE 8—PER CAPITA AVAILABILITY OF SELECTED ARTICLES OF CONSUMPTION IN INDIA

Year	Edible Oils , kg.	Vanaspati, kg.	Sugar (Nov.-Oct.), kg.	Cotton Cloth m	Man-made Fibre Fabrics†† (metres)	Tea, g.	Coffee*, g.	Electricity** (domestic use), kWh
1955-56	2.5	0.7	5.0	14.4	N.A.	2.57	67	2.4*
1960-61	3.2	0.8	4.7	13.8	1.2	287	80	3.4
1961-62	3.2	0.7	5.8	14.8	1.2	309	57	3.8
1962-63	3.1	0.8	5.4	14.4	1.2	294	72	4.2
1963-64	2.7	0.8	4.9	14.7	1.2	298	76	4.4
1964-65	3.6	0.8	5.1	15.2	1.6	309	78	4.7
1965-66	2.6	0.8	5.7	14.7	1.7	337	70	4.8
1966-67	2.5	0.7	5.1	14.0	1.7	365	85	5.2
1967-68	3.2	0.8	4.3**	13.6	1.7	351	53	5.7
1968-69	2.4	0.9	5.0	14.4	1.9	353	75	6.0
1969-70	2.8	0.9	6.1	13.6	1.8	377	59	6.5
1970-71	3.3	1.0	7.3	13.6	1.7	387	113	7.0
1971-72	2.9	1.1	6.7	12.4	1.7	392	45	7.3
1972-73P	2.0	1.0	6.1	13.2	1.6	402	69	N.A.

(P) = Provisional

† Includes groundnut oil, rapeseed and mustard oil, coconut oil and sesamum oil but excludes oil used for manufacture of vanaspati. In the absence of figures for coconuts for 1972-73, the figures for 1971-72 have been repeated.

†† Relates to calendar years: figures for 1955 are shown against 1955-56 and so on.

* Figures relate to Coffee season From 1967-68 the sugar season is Oct.-Sept. ** Relates to 1956.

[Records & Statistics, Quart. Bull. East Econ., 25 (2) (1974), 81]

TABLE 9—STATE-WISE ESTIMATES OF PRODUCTION OF FOODGRAINS

(Thousand Tonnes)

State	Year	Rice	Wheat	Coarse Cereals		Total Cereals	Total Pulses	Total Food-grains
				Jowar Bajra & Maize	Others			
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Andhra Pradesh	1971-72	4717.1	10.8	1661.3	521.7	6910.9	379.6	7290.5
	1972-73	3643.7	6.3	1419.9	302.9	5372.8	235.5	5608.3
Assam	1971-72	1908.1	48.0	6.4	2.9	1965.4	30.9	1996.3
	1972-73	2177.1	160.4	5.9	4.9	2348.3	48.0	2396.3
Bihar	1971-72	5273.2	2493.7	139.4	271.3	8177.6	889.3	9066.9
	1972-73	4464.5	3136.4	811.6	250.8	8663.3	656.0	9319.3
Gujrat	1971-72	517.5	897.4	2459.8	186.0	4060.7	161.3	4222.0
	1972-73	147.9	547.6	1312.8	94.1	2102.4	112.0	2214.4
Haryana	1971-72	536.0	2402.0	808.0	115.1	3861.1	684.3	4545.4
	1972-73	466.0	2160.0	618.0	143.0	3387.0	561.2	3948.2
Himachal Pradesh	1971-72	103.6	394.5	330.3	87.8	916.2	29.1	945.3
	1972-73	85.7	365.0	392.8	57.6	901.1	27.7	928.8
Jammu & Kashmir	1971-72	370.1	168.0	374.3	17.1	929.5	29.1	958.6
	1972-73	342.7	168.0	389.6	18.2	918.5	27.0	945.5
Karnataka	1971-72	2097.1	187.2	2343.6	970.5	5598.4	466.1	6064.5
	1972-73	1748.8	109.2	1586.0	917.1	4361.1	238.9	4600.0
Kerala	1971-72	1351.7	...	0.8	7.6	1360.1	13.1	1373.2
	1972-73	1339.8	...	0.6	7.5	1347.9	13.3	1361.2
Madhya Pradesh	1971-72	3702.4	3189.2	1847.5	542.1	9281.2	2353.1	11634.3
	1972-73	3345.0	2447.2	2221.1	484.5	8497.6	2174.6	10672.2
Maharashtra	1971-72	1368.5	502.8	2188.8	249.9	4310.0	642.9	4952.9
	1972-73	745.8	248.5	1465.7	139.7	2599.7	451.0	3050.7
Manipur	1971-72	158.6	4.2	17.1	...	179.9	...	179.9
	1972-73	152.2	4.2	22.0	...	178.4	...	178.4
Meghalaya	1971-72	108.0	0.2	7.5	0.9	116.6	0.9	117.5
	1972-73	106.6	0.2	7.5	0.9	115.2	0.9	116.1
Nagaland	1971-72	33.2	...	...	...	33.2	...	33.2
	1972-73	30.1	...	...	...	30.1	...	30.1
Orissa	1971-72	3619.5	38.7	79.6	225.8	3963.6	390.2	4353.8
	1972-73	3978.5	84.2	66.8	233.8	4363.3	390.8	4754.1
Punjab	1971-72	920.0	5618.0	1029.8	55.3	7623.1	305.2	7928.3
	1972-73	955.0	5361.0	1907.8	59.0	7382.8	294.3	7677.1
Rajasthan	1971-72	159.4	1888.7	2366.9	602.1	5017.1	1307.7	6334.8
	1972-73	79.9	1749.3	1828.1	495.6	4152.9	999.3	5152.2
Tamil Nadu	1971-72	5302.0	0.7	826.1	660.6	6789.4	153.7	6943.1
	1972-73	5384.0	0.8	796.1	608.1	6789.0	173.1	6962.1
Tripura	1971-72	270.8	0.9	...	...	271.7	1.4	273.1
	1972-73	183.3	0.9	...	...	184.2	0.9	185.1
Uttar Pradesh	1971-72	3776.5	7550.1	1599.7	1851.3	14777.6	2919.9	17697.5
	1972-73	3248.2	7633.3	2439.0	1836.3	15156.8	2793.1	17949.9
West Bengal	1971-72	6508.4	921.2	38.2	71.1	7538.9	317.0	7855.9
	1972-73	5747.2	652.7	38.7	45.8	6484.4	284.8	6769.2
All India	1971-72	43068.0	26409.9	18141.5	6454.9	94074.3	11093.4	105167.7
	1972-73	38632.8	24922.6	16443.7	5714.2	85713.3	9487.9	95201.2

Note:—Production estimates for 1971-72 and 1972-73 are provisional and subject to revision.

[Records & Statistics, Quart. Bull. East. Econ., 25 (2) (1974), 83]

TABLE 10—WHEAT: AREA AND PRODUCTION, 1961-65, 1971, 1972, AND 1973¹

Country (1)	Area				Production			
	1961-65 (2)	1971 (3)	1972 (4)	1973 ¹ (5)	1961-65 (6)	1971 (7)	1972 (8)	1973 ¹ (9)
	1 000 hectares				1 000 metric tons			
WORLD	210 894	216 524	213 868	224 350	254 302	353 826	347 581	364 970
<i>Africa</i>	7 656	8 534	9 133	8 710	6 331	8 940	9 724	9 210
Algeria	1 969	1 946	2 403	2 000F	1 254	1 235	1 692	*1 400
Egypt	557	567	521	...	1 459	1 729	1 616	...
<i>North & Central America</i>	31 398	27 875	28 469	32 480	49 985	60 495	58 264	65 480
Canada	11 145	7 854	8 640	10 010	15 364	14 412	14 514	16 450
Mexico	784	697	655	700F	1 549	2 019	1 672	2 000F
United States	19 432	19 293	19 142	21 739	33 040	44 030	42 043	47 002
<i>South America</i>	7 385	8 020	7 231	7 250	10 048	9 833	10 415	9 360
Argentina	4 916	4 315	4 965	4 000F	7 541	5 680	7 900	6 000F
Brazil	812	2 261	1 000F	2 000F	574	2 132	800F	2 000F
<i>Asia</i>	62 451	73 001	74 767	76 180	55 912	85 618	94 077	94 140
Afghanistan	2 321	2 350	2 400F	...	2 207	1 915	2 950	...
China	25 175F	28 500F	28 700F	...	22 230F	32 500F	34 500F	...
India	13 402	18 241	19 163	21 200F	11 191	23 833	26 477	30 000F
Israel	58	113	109	100F	90	200	301	200F
Japan	572	166	114	70	1 332	441	284	190F
Jordan	268	244	*210	*186	180	168	211	*95
Korea Rep. of	138	142	*130	*127	277	322	241	*235
Pakistan	4 984	5 978	5 797	6 350F	4 152	6 476	6 891	7 520
<i>Europe</i>	28 576	27 826	27 889	27 220	59 348	81 347	82 173	80 370
Austria	276	274	274	271	704	974	863	880F
Belgium ²	215	202	211	*190	826	915	950	850F
Denmark	130	121	135	117	535	585	591	540F
France	4 265	3 978	3 958	3 952	12 495	15 482	18 123	17 242
German Dem.Rep.	430	633	690	...	1 357	2 490	2 744	...
Germany, Fed. Rep. of ²	1 391	1 544	1 626	1 599	4 607	7 142	6 608	6 650F
Greece	1 193	979	904	*865	1 765	1 906	1 773	*1 800
Ireland	104	90	64	*52	343	380	*251	*213
Italy	4 398	3 910	3 821	3 670	8 857	9 994	9 423	8 857
Netherlands	138	142	156	138	606	710	673	650F
Poland	1 516	2 061	2 050	*2 250	2 988	5 456	5 147	5 900F
Sweden	264	246	266	*290	909	995	1 150	*1 200
United Kingdom	870	1 097	1 127	1 160F	3 520	4 815	4 760	4 800F
Yugoslavia ²	2 006	1 930	1 925	1 686	3 599	5 605	4 844	*4 700
<i>Oceania</i>	6 806	7 234	7 886	9 210	8 470	8 834	6 978	11 410
Australia	6 726	7 138	7 770	*9 100	8 222	8 510	6 551	11 000F
New Zealand	80	96	116	114	248	324	427	408
U.S.S.R.	66 622	64 035	58 492	63 300	64 207	98 760	85 950	*95 000
<i>Developed Market Economies</i>	9 715	55 172	56 334	60 690	103 697	126 267	121 936	130 950
North America	30 577	27 146	27 782	31 750	48 404	58 442	56 557	63 450
Western Europe	20 505	19 093	18 993	18 080	44 562	56 681	56 088	53 900
Oceania	6 806	7 234	7 886	9 210	8 470	8 834	6 978	11 410
Other developed market economies	1 828	1 699	1 673	1 650	2 262	2 310	2 314	2 190
<i>Developing Market Economies</i>	50 820	59 590	60 925	61 800	49 036	71 230	78 752	76 910
Africa	5 725	6 370	6 917	6 490	3 961	5 360	6 155	5 560
Latin America	8 206	8 749	7 919	7 980	11 629	11 886	12 123	11 400
Near East	18 109	19 693	20 601	19 250	17 610	23 005	26 545	21 860
Far East	18 780	24 779	25 487	28 080	15 835	30 980	33 929	38 090
<i>Central Planned Economies</i>	100 360	101 762	96 609	101 860	101 569	156 329	146 892	157 110
Asia	25 666	28 994	29 221	29 420	22 576	32 903	34 857	35 650
Europe and U.S.S.R.	74 694	72 768	67 388	72 440	78 993	123 426	112 035	121 460

¹1973, Preliminary figures;²Includes spelt; F=FAO Estimate;

[Monthly Bull. of Agri. Econ. & Statis., FAO, 22 (9) (1973), 19]

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The kinetics of the reaction of gaseous hydrogen sulphide with zinc oxide-ferric oxide and zinc oxide-copper oxide systems have been investigated in the range 200-400°C. With increasing temperature, the reaction rate increased in zinc oxide-ferric oxide system, whereas in zinc oxide-copper oxide it passed through a peak and above 300°C showed a negative temperature dependence. Elovich kinetics have been used to explain the hydrogen sulphide pick-up by both the systems. The apparent energy of activation was calculated and correlated with the gas absorption values. The rate equations developed from kinetic data are:

$$\frac{dq}{dt} = \exp(0.56) \exp\left(114 - \frac{11.2}{RT}\right) \times 10^{-3} q \text{ for ZnO-Fe}_2\text{O}_3 (T = 200-400^\circ\text{C})$$

$$\frac{dq}{dt} = \exp(0.09) \exp\left(43.7 - \frac{121.4}{RT}\right) \times 10^{-4} q \text{ for ZnO-CuO } (T = 200-300^\circ\text{C})$$

$$\frac{dq}{dt} = \exp\left(-233 + \frac{25.7}{RT}\right) \times 10^{-3} q \text{ for ZnO-CuO } (T = 300-400^\circ\text{C})$$

Kinetics of the Reaction of Hydrogen Sulphide with Zinc Oxide - Ferric Oxide and Zinc Oxide - Copper Oxide Systems

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Introduction

Zinc oxide absorbs hydrogen sulphide to form zinc sulphide and water, in an irreversible reaction which has been utilized here for removal of traces of sulphur from industrial gases in the range 200-400°C. The removal probably takes place through absorption, followed by chemical reaction between absorbate and absorbent. This removal from feed is necessary because sulphur compounds above certain limits can greatly damage the catalyst activity for dehydrogenation¹, hydrogenation of olefines and cracking hydrocarbons².

Chemisorption of sulphur and sulphur compounds by catalysts and their kinetics have been studied by a number of workers³⁻⁵. Chemisorption is very akin to chemical reaction, the difference being that here the formation of the bond between absorbate and absorbent is limited to the atoms on the surface of the adsorbent only, the bulk of the material not participating in the process. It is possible that the above mechanism in-

volved in the process of chemisorption may be extended to a similar process taking place in the bulk phase of the adsorbent and identical kinetics may govern the absorption in both the processes. This argument probably justified the application of Elovich equation to bulk reaction and may explain the reaction kinetics of hydrogen sulphide on metallic oxides.

The kinetics of chemisorption of gases by solids and application of Elovich kinetics have been studied⁶⁻¹⁰ extensively. Recently, a similar application of Elovich kinetics to explain the reaction of hydrogen sulphide with supported and unsupported nickel oxide has been made by Dorer¹¹. Massoth and Bidlack¹² studied the sulphiding of tungsten oxide, bulk and supported on silica and alumina, and the kinetic data were correlated with a logarithmic type growth law derived on the basis of pore blocking model. The logarithmic equation is mathematically equivalent to the Elovich equation although the theoretical basis is entirely different.

In this laboratory a number of workers¹³⁻¹⁵ studied the hydrogen sulphide absorption by zinc oxide and tried to correlate the absorption characteristics with physico-chemical properties, like surface area, pore size distribution and heat treatment. These studies revealed the influence of the preparative technique and structural properties on the activity and sulphur retention capacity. But information on the kinetics of absorption of hydrogen sulphide by zinc oxide-ferric oxide and zinc oxide-copper oxide system and their surface heterogeneity is not available in literature. The present study aims to characterize the zinc oxide—ferric oxide and zinc oxide-copper oxide systems from kinetics of hydrogen sulphide adsorption. Both the systems follow similar reaction trend and obey Elovich kinetics¹⁶. Surface heterogeneity of both the systems was clearly established.

Experimental

Sample Preparation: The chemicals used in the preparation were of A. R. quality.

(i) **Zinc Oxide—Ferric Oxide ($\text{ZnO-Fe}_2\text{O}_3$)**—Zinc oxide was dissolved in nitric acid and to this ferric nitrate solution equivalent to approximately 2.0 per cent of ferric oxide in the product was added. The temperature of the solution was maintained at 50°C. The zinc and ferric carbonates were coprecipitated by a 10 per cent solution of ammonium bicarbonate. The precipitate was filtered, washed, repulped and again filtered, washed with distilled water in order to remove nitrate as well as other soluble impurities. The cake was dried at 400°C for 4 hours and the resultant product was shaped in 1-2 mm. size globules with water spraying.

(ii) For zinc oxide-copper oxide sample the process was same except in place of ferric nitrate, copper-nitrate solution equivalent to 1 per cent copper oxide in the dry mixed oxide was added.

Reaction with Hydrogen Sulphide: The absorption of hydrogen sulphide by the two samples were measured in a flow system at atmospheric pressure (Fig. 1). The feed gas ($\text{N}_2 + \text{H}_2\text{S}$) containing 8000-10,000 ppm. hydrogen sulphide as sulphur was passed in a down-flow direction through the catalyst bed. The hydrogen sulphide was 70-80 per cent pure, prepared from ferrous sulphide and dilute sulphuric acid. After measuring the purity, a calculated amount of the gas was mixed with nitrogen and then injected into the system through a measuring device. In each case, 10 c.c. of the catalysts (1-2 mm.) was loaded in a glass reactor along with enough pyrex beads (1-2 mm.) to fill a total volume of

50 ml. The bed was maintained at the required temperatures viz. 200, 300, 350 and 400°C, by regulating the voltage to the heater circuit. The catalyst bed tempera-

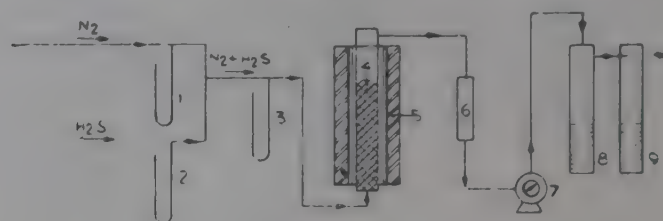


Fig. 1—Sketch of the Apparatus
Legend

1, 2 & 3 Manometers, 4, Catalyst, 5. Electric Furnace, 6. Glass wool, 7. Gasmeter, 8 & 9. Cadmium Acetate Bubbler

ture in the upper and lower zones, measured by a pyrometer, did not differ beyond $\pm 2^\circ\text{C}$, and the rate of hydrogen sulphide pick-up was measured at variable space velocities, viz. 7000, 8000 and 9000 v/v/hr. keeping the bed temperature constant. The range of space velocity was chosen with a view to get a measurable amount of sulphur in the outlet and also to ensure uniform spread of the reaction throughout the bed. The gas leaving the reactor was then passed through a glass wool filter and later it was scrubbed through two bottles containing acidic cadmium acetate solution for the estimation of the unabsorbed hydrogen sulphide.

Results and Discussion

Zinc oxide constituted over 98 per cent in both the catalyst systems, the concentration of ferric oxide and copper oxide being 1 to 2 per cent. The minor constituents were added to increase the mechanical strength of the granules and reduce their dusting losses. Ferric oxide and copper oxide also reacted chemically with hydrogen sulphide and so addition of these oxides was not likely to change the effectiveness of zinc oxide for hydrogen sulphide removal. The rate of hydrogen sulphide pick-up by the oxide catalysts has been followed by measuring the concentrations of sulphur in the feed and effluent gas at definite intervals.

The uptake of hydrogen sulphide as a function of temperature and time is shown in Figs. 2-5. The rate of adsorption of hydrogen sulphide increased with temperature in zinc oxide-ferric oxide system whereas in zinc oxide-copper oxide system it increased up to 300°C and then decreases with increasing temperature. It can be observed that with increased coverage the rate of hydrogen sulphide pick-up by both systems declines at all temperatures. Zinc oxide copper oxide system was relatively less active than the zinc oxide-ferric oxide system and its activity dropped more sharply with in-

creased volume of hydrogen sulphide absorption. Attempts have been made here to analyse the observed data with the help of Elovich kinetic law, which has general application to chemisorption kinetics. Elovich equation has also been successfully utilized to interpret hydrogen sulphide absorption by metallic oxides. A reasonable interpretation of Elovich equation when

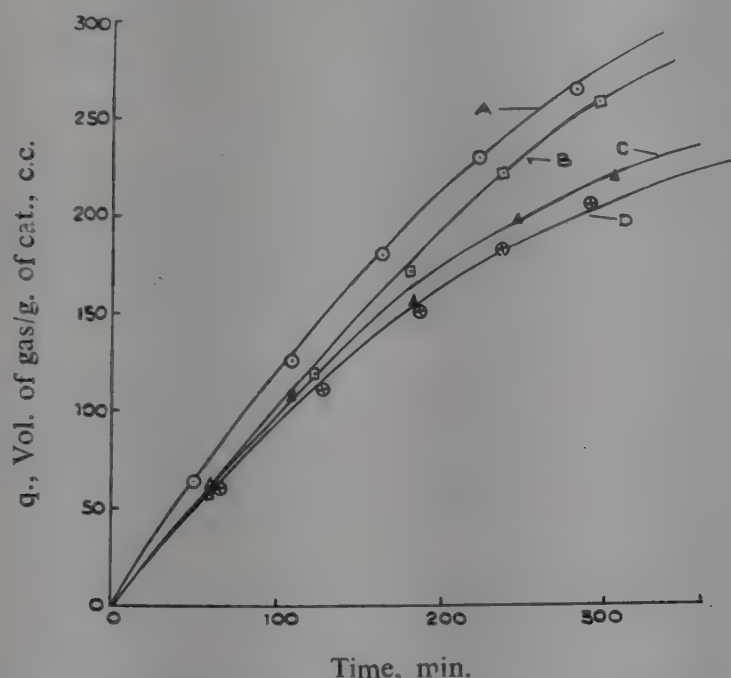


Fig. 2—Zinc Oxide-Ferric Oxide System
A-400°C, B-350°C, C-300°C, D-200°C

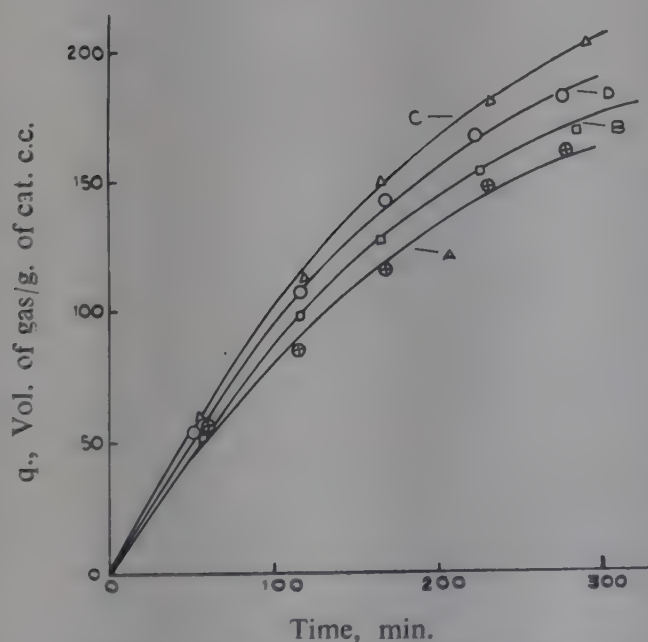


Fig. 3—Zinc Oxide-Copper Oxide System
A-400°C, B-350°C, C-300°C, D-200°C

applied to rate processes on heterogeneous surface, where a is a constant independent of q , and is related to the spread in activation energy over the surface^{6,15} is as follows :

$$\frac{dq}{dt} = a e^{-\alpha q} = a \exp(-\alpha q) \quad (1)$$

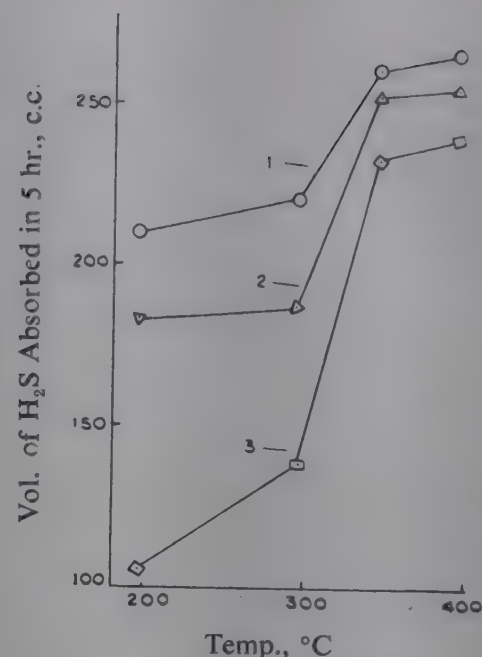


Fig. 4—Zinc Oxide-Ferric Oxide System
1. 9000, 2. 8000, 3. 7000 (Space Velocity)

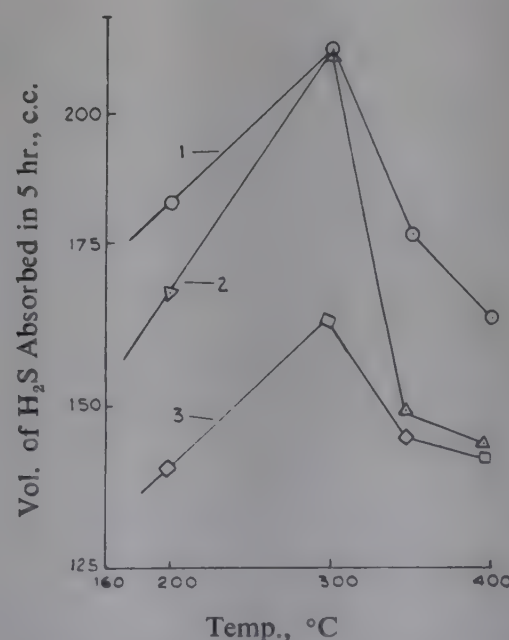


Fig. 5—Zinc Oxide-Copper Oxide System
1. 7000, 2. 8000, 3. 9000 (Space Velocity)

It has been shown that a sum of simultaneously occurring independent first or second order reactions will approximate Elovich kinetics. Had the reaction of hydrogen sulphide with zinc oxide been of zero order, the activation energy would have a linear function of the extent of reaction, Elovich kinetics obeyed exactly and α equalled to the spread in the activation energy. The plots of θ , the fraction of zinc oxide converted to zinc sulphide, with time were straight line, (Figs. 6 and 7), which showed the applicability of Elovich equation in systems under study. As the significance of Elovich equation has been thoroughly discussed in a numbers of papers^{6,11,17} further elaboration is not necessary.

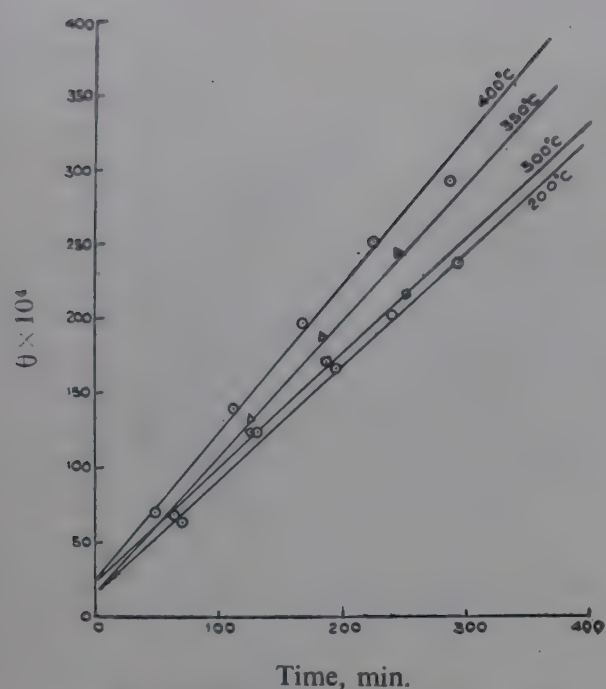


Fig. 6—Zinc Oxide-Ferric Oxide System

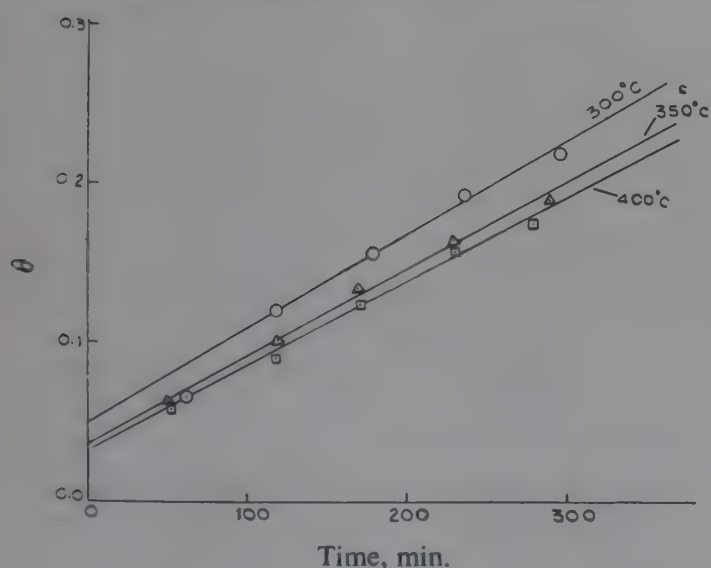


Fig. 7—Zinc Oxide-Copper Oxide System

Apparent Energy of Activation of Zinc Oxide—Ferric Oxide and Zinc Oxide—Copper Oxide : The apparent activation energy (E_a) as a function of the extent of reaction (q) can be obtained from the experimental data by using the relation :

$$\frac{dq}{dt} = a \exp(-\alpha q)$$

$$= A(q) \exp[-E(q)/RT] = \text{rate} \quad (2)$$

$$\text{Log (rate)} = \log a - q = \log A(q) - \frac{E(q)}{RT}$$

The parameters a and q can be obtained from the data in Figs. 1 & 2. The calculation of rates for these systems at different temperatures has been done with the help of Figs. 2 and 3. The values of t are taken as the mean of t_1 and t_2 and similarly q values are taken as the mean q_1 and q_2 . The plots of rate $\frac{dq}{dt}$ vs. time and

rate vs q are linear. The values of the rate (dq/dt) at constant values of q at different temperatures were determined with the help of the plots of dq/dt vs q . These figures have not been included in this paper. The plots of $\log(\text{rate})$ vs $\frac{1}{T}$ for constant values of q were linear (Figs 8—9). The observed energies of activation

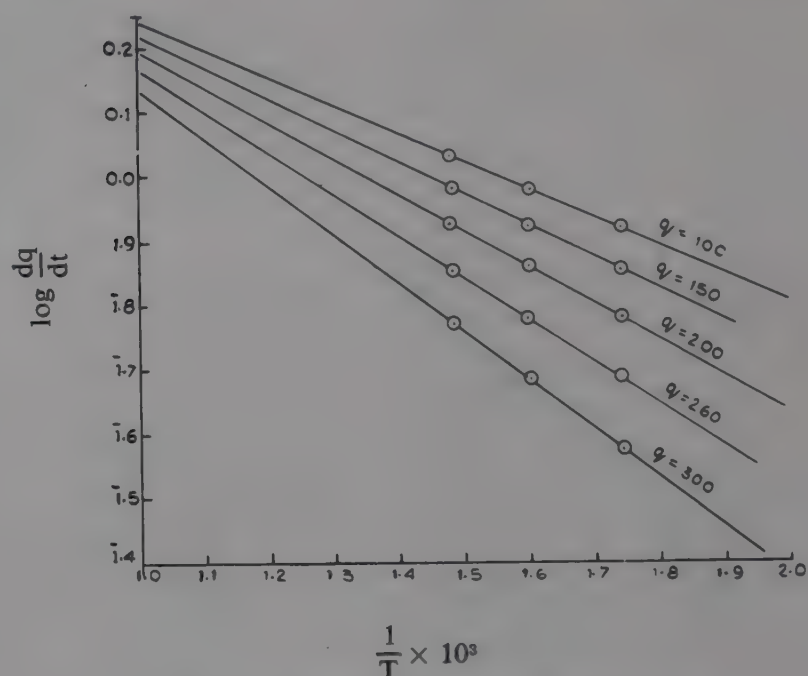


Fig. 8—Zinc Oxide-Ferric Oxide System

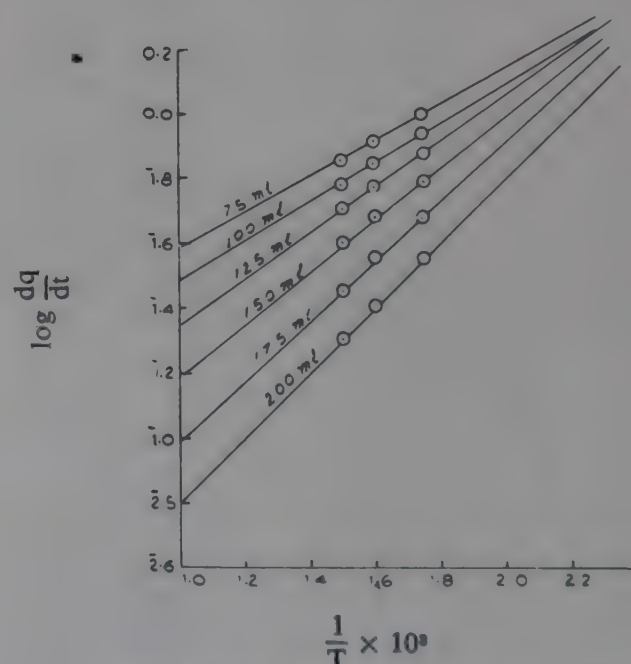


Fig. 9—Zinc Oxide-Copper Oxide System

for zinc oxide—ferric oxide system calculated from the slope of Fig. 7, were in the range of 2.05-3.5 K cal/mole for q value varying from 100 to 300 ml. Similarly, for zinc oxide-copper oxide system energy of activation calculated from the slope (fig. not given) are 1.58 to 4.35 K cal/mole in the range 200-300°C and for q value varying from 50-200 ml. but E_a value calculated from

the slopes of Fig. 9 for the same catalyst varied from -2.58 to -5.2 K cal/mole in the range $300-400^{\circ}\text{C}$ for q values varying from 75 to 200 ml. For zinc oxide-ferric oxide system the apparent energy of activation positive, whereas for zinc oxide-copper oxide system it was negative in the range $300-400^{\circ}\text{C}$., which indicated that the rate of absorption (dq/dt) decreased with the increase in the temperature. The decrease of rate above 300°C in the case of zinc oxide-copper oxide system was somewhat unexpected. It might have been caused by internal diffusion restriction which might become a prominent factor at a higher temperature for a system with higher aggregate of finer pores. But in the present investigation, the size of the samples was 1-2 mm. where the diffusion restriction should not have significant influence on the reaction kinetics.

When apparent energy of activation was plotted against q values, a straight line passing through the origin was obtained but the points corresponding to lower values of q were deviating from the origin (Fig. 10), which showed that in the initial period of absorption of hydrogen sulphide, Elovich kinetics did not apply satisfactorily. From the estimated values, it is seen that deviation from Elovich kinetic occurred when the surface coverage, i.e. θ value, was less than 0.02 and 0.018 for zinc oxide-ferric oxide and zinc oxide-copper oxide respectively. The faster rate of absorption at low surface coverage at the initial stages might be the cause for this deviation from Elovich kinetics.

Empirical Rate Equation: An empirical relation between the apparent activation energy E_a and volume of hydrogen sulphide reacted with zinc oxide systems can be worked out with the help of the Fig 10.

For zinc oxide-ferric oxide system $E(a) = 0.0122 q \dots (3)$

and for zinc oxide-copper oxide, $E(a) = 0.01214 q$
($T = 200-300^{\circ}\text{C}$) $\dots (4a)$

$E(a) = 0.025 q$ ($T = 300-400^{\circ}\text{C}$) $\dots (4b)$

The intercept for $1/T \longrightarrow 0$ of linear plots of $\log(\text{rate})$ vs. $1/T$ (Figs. 7 & 8) as governed by equation (2) equalled to $\log A(q)$. It was found that these intercepts have functional dependence on q of the form as detailed in Fig. 10. In case of zinc oxide-ferric oxide system $A(q)$ increased with increasing absorption. Contrary to this, the effect of increased surface coverage has the reverse trend on zinc oxide-copper oxide. The numerical value of $A(q)$ decreased with increasing amount of hydrogen sulphide, picked-up by the oxide.

For zinc oxide-ferric oxide $\log A(q) = 0.56$
 $+ 144 \times 10^{-3} q \dots (5)$

and for zinc oxide-copper oxide it will be

$\log A(q) = 0.09 + 43.7 \times 10^{-4} q$
($T = 200-300^{\circ}\text{C}$) $\dots (6a)$

and $\log A(q) = 233 \times 10^{-3} q$ ($T = 300-400^{\circ}\text{C}$) $\dots (6b)$

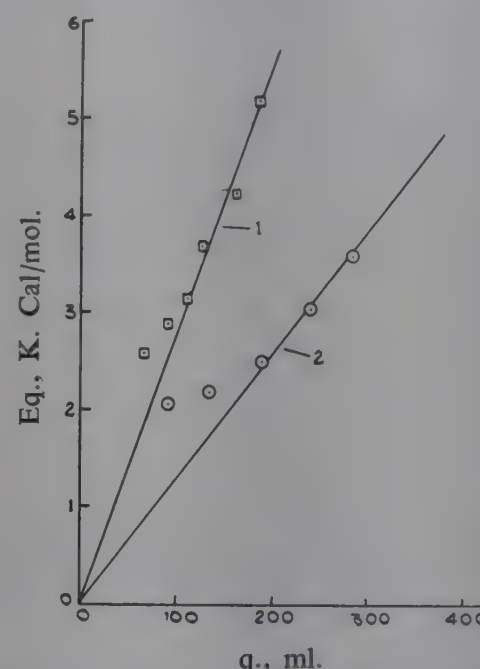


Fig. 10—Relation between Apparent Energy of Activation and Extent of Reaction
1. ZnO-CuO 2. ZnO-Fe₂O₃

Of course $\log A(q)$ must be linearly dependent or independent of q if the overall kinetic expression were of the Elovich form. The equations 5, 6a and 6b showed clearly that $\log A(q)$ is linearly dependent on the volume of hydrogen sulphide absorbed by both the systems. This in turn proved again the applicability of Elovich form of expression to characterize a process, basically a chemical reaction between a gaseous and a solid phase as observed by Dorer¹¹.

The rate of reaction of hydrogen sulphide with these catalysts can then be expressed as

For zinc oxide-ferric oxide $\log \left(\frac{dq}{dt} \right) = 0.56$
 $+ 114 \times 10^{-3} q - \frac{11.2 \times 10^3 q}{RT}$

hence $\log a = 0.56$

and

$$-\alpha = \left(114 - \frac{11.2}{RT} \right) 10^{-3}$$

$$\left(\frac{dq}{dt} \right) = \exp(0.56) \exp \left(114 - \frac{11.2}{RT} \right) 10^{-3} q \quad (7)$$

Similarly, for zinc oxide-copper oxide system

$$\log \left(\frac{dq}{dt} \right) = 0.09 + 43.7 \times 10^{-4} q - \frac{121.4 \times 10^4 q}{RT}$$

($T = 200-300^\circ\text{C}$)

$$\log a = 0.09$$

$$\text{and } -\alpha = \left(43.7 - \frac{121.4}{RT} \right) 10^{-4}$$

$$\frac{dq}{dt} = \exp(0.09) \exp \left(43.7 - \frac{121.4}{RT} \right) 10^{-4} q \quad (8)$$

$$\text{and } \log \frac{dq}{dt} = 233 \times 10^{-3} q + \frac{25.7 \times 10^{-3} q}{RT}$$

($T = 300-400^\circ\text{C}$)

$$\text{hence } \log a = 0$$

$$\text{and } -\alpha = \left(-233 + \frac{25.7}{RT} \right) 10^{-3}$$

$$\left(\frac{dq}{dt} \right) = \exp \left(-233 + \frac{25.7}{RT} \right) 10^{-3} q \quad (9)$$

All the three equations 7, 8 and 9 have identical forms differing only in the value of A. and the exponential factor.

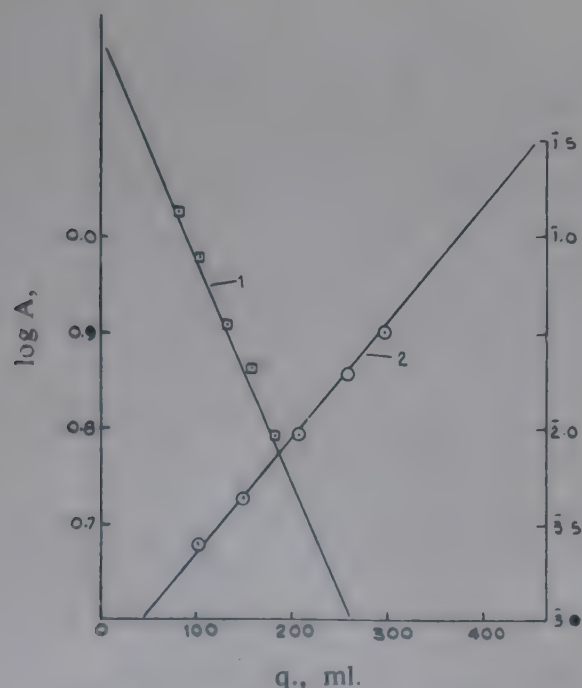


Fig. 11—1. ZnO-CuO, 2. ZnO-Fe₂O₃

Conclusions

From the experimental findings, the following can be concluded: (i) the surface of the precipitated zinc oxide-ferric oxide and zinc oxide-copper oxide are heterogenous energetically; (ii) the initial sulphidation of the surface with dry hydrogen sulphide takes place rapidly and then slows down; (iii) sulphidation with bulk oxides at θ values above 0.02 proceeds slowly and the process obeys Elovich kinetics in the temperature range 200-400°C; (iv) activation energy varies from 2.05 cal/mole to 3.5 K cal/mole for zinc oxide-ferric oxide in ($T=200-400^\circ\text{C}$) at q values corresponding to 100 to 300 ml. Similarly for zinc oxide-copper oxide system activation energy are 1.58 to 4.35 K cal/mole ($T=200-300^\circ\text{C}$) and -2.58 to 5.2 K cal/mole ($T=300-400^\circ\text{C}$) at corresponding q values of 75 ml—200 ml and 50 ml—200 ml hydrogen sulphide absorption respectively and (v) above 300°C sulphidation rate shows a negative temperature dependence with zinc oxide—copper oxide system.

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In order to determine the optimum doses of phosphorus, zinc and combination of zinc and phosphorus in wheat, a trial was undertaken at Sindri (soil pH=8.2) with randomized block design having three replications. The doses of phosphorus and zinc corresponded to 0, 20, 40, 80 kg/ha of phosphorus and 0, 5, 10, 15 ppm of zinc respectively. Significant differences in grain yield were observed within levels phosphorus, zinc and phosphorus X zinc. The response due to levels of phosphorus when averaged over levels of zinc was found in the following order: $P_3 = P_2 > P_1$. The response due to levels of zinc when averaged over phosphorus levels was seen as $Zn_1 = Zn_2 > Zn_3$. P_2, Zn_1 combination produced the highest yield and found significantly superior to other treatment combinations. Zinc application at the highest level (Zn_3) depressed the yield significantly, indicating a possible imbalance in phosphorus uptake at higher level of zinc.

Effect of Phosphorus and Zinc on Grain Yield of Wheat

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Introduction

With the introduction of high-yielding varieties of crops and adoption of multiple cropping system, the deficiency of some of the micronutrients, particularly zinc, has become widespread in many parts of India. Gupta *et al*¹ observed that some of the soils of the wheat-growing tracts in this country were severely to marginally zinc deficient and their phosphorus status was also far from satisfactory. It was, therefore, likely to get an optimum wheat yield with the application of phosphorus and zinc in these wheat-growing tracts. Moreover, the fact that phosphorus induces zinc deficiency is known to occur in several crop plants²⁻⁴. The interaction of zinc and phosphorus in calcareous soils are also reported by Lindsay *et al*⁵. In view of these findings, much of the current attention is now concentrated on determining the effect of phosphorus fertilization on the zinc nutrition of plants⁶. However, in view of the reciprocal antagonism that these two nutrients exhibit, it is equally important to study the reverse effect, i.e. of zinc on phosphorus uptake¹. In the context of the above discussion, the present experiment was undertaken to study phosphorus and zinc fertilization on wheat.

Experimental

The experiment having 16 treatment combinations and three replications were designed in randomized blocks in the FCI's farm at Sindri, the net size of each plots being 11.25 sq. m. The soil of this farm was alluvial in nature having loamy texture. The chemical

analysis of a typical soil sample gave pH 8.2, total phosphorus 0.031 per cent, available phosphorus 12.6 ppm. and dithizone extractable zinc 0.53 ppm. The doses for phosphorus and zinc corresponded to 0(P_0), 20(P_1), 40(P_2) and 80(P_3) kg. P/ha and 0(Zn_0), 5(Zn_1), 10(Zn_2) and 15(Zn_3) ppm of zinc respectively. Ammonium sulphate and muriate of potash were applied uniformly as basal dose at the rate of 80 kg. of nitrogen and 40 kg. of potassium oxide (K_2O) per ha respectively in all the plots. The requisite quantities of phosphorus in the form of superphosphate were applied in the randomly allocated plots and mixed thoroughly. The seeds (var. *Sonalika*) were sown in lines with the help of a seed drill. Zinc sulphate was sprayed at 20 days period of crop growth.

Results and Discussion

The results show significant differences in grain yield within levels of phosphorus, levels of zinc and phosphorus x zinc. The effect due to different levels of phosphorus on grain yield, when averaged over levels of zinc, can be shown as below :

$$P_3, P_2; P_1, P_0$$

There was no significant difference within P_2 and P_3 levels, when averaged over levels of zinc, and both of these levels were significantly superior to the P_1 level, the average response being 5.99 q/ha. The P_1 level also produced significantly higher yield over the P_0 level, the average response being 4.78 q/ha. This suggests that the effect due to increase in level of phosphorus was

very prominent upto a limit of 40 kg. p/ha after which the rate of increase in yield was almost insignificant (Fig. 1). The effects due to different levels of zinc on grain yield, when averaged over levels of phosphorus, can be arranged as below : Zn_1 , Zn_2 , Zn_0 , Zn_3 .

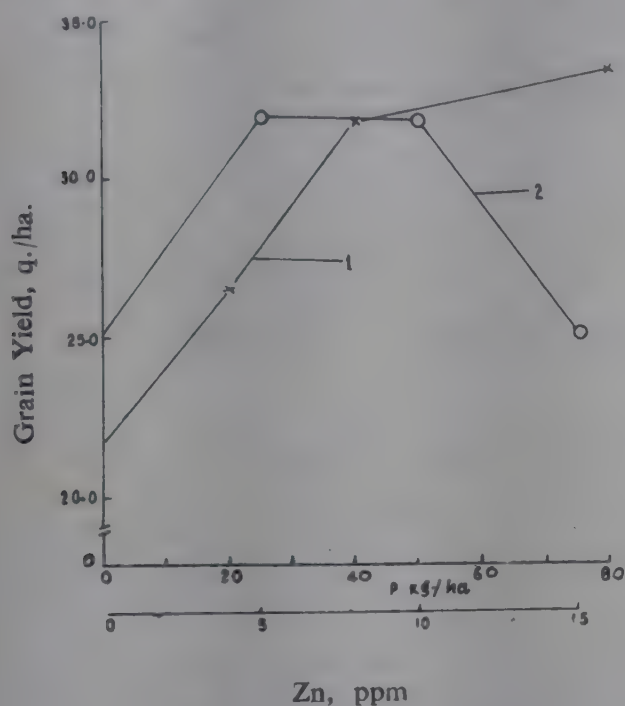


Fig. 1—Effect of Increase in Level of Zinc and Phosphorus on Grain Yield

1. Effect of Phosphorus, 2. Effect of Zinc.

The grain yield increased significantly with the first increment of zinc level (Zn_1), the average response being 6.65 q./ha. Further increase in the level definitely depressed the yield, and this decrease was significant at Zn_3 level (Table 1 ; Fig. 1). It was likely that the higher doses of zinc produced some physiological imbalances in phosphorus uptake and nutrition of the plants.

TABLE 1—EFFECT OF PHOSPHORUS AND ZINC ON GRAIN YIELD OF WHEAT, q./ha.

Levels of Zinc	Zn No	Zn_1 5 ppm	Zn_2 10 ppm	Zn_3 15 ppm	Mean
Levels of Phosphorus	Zinc				
P_0 (No P)	15.57	25.07	27.92	18.75	21.82
P_1 (20 kg.P/ha)	28.17	28.25	28.00	22.00	26.60
P_2 (40 kg.P/ha)	27.12	41.25	33.42	25.67	31.86
P_3 (80 kg.P/ha)	30.50	33.42	35.67	33.82	33.32
Mean	25.34	31.99	31.25	25.06	—

C.D. at 0.05 level: For P means=2.55, For Zn means=2.55, For $P \times Zn$ =5.10

The effects due to zinc x phosphate on grain yield was also significant. At the Zn_0 level, yield increased prominently at the P_1 level. At the Zn_1 and Zn_2 levels, increase in yield was most prominent at the P_2 level, while at the Zn_3 level this increase was marked at the P_3 level (Fig. 2). Of the two nutrient elements tested, phosphorus was the main limiting factor. At the Zn_0 level, yield was increased significantly with the first increment of phosphate level possibly due to correction of low supply of phosphorus. After this no appreciable increase was noted suggesting a possible limiting effects of zinc. This can be further evidenced from the higher recorded yield at the P_2 Zn_1 level. At the P_0 level,

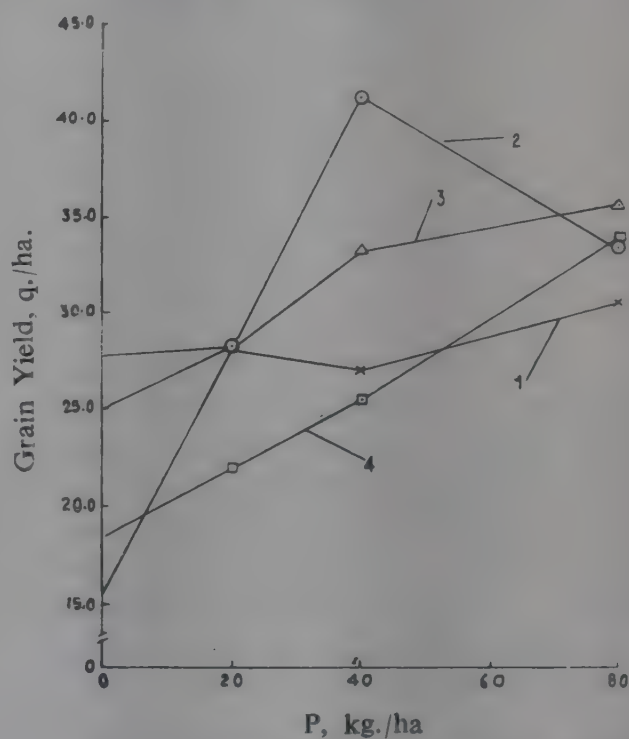


Fig. 2—Effect of Phosphate on Grain Yield
1. Zn_0 , 2. Zn_1 , 3. Zn_2 , 4. Zn_3

yield increased significantly with the first increment of zinc level indicating a definite positive effect of zinc on wheat yield. Further addition of zinc depressed the yield at all the levels of phosphorus indicating a repressive effect of zinc on phosphorus uptake.

It was further interesting to note that the yield decreased with the addition of the highest dose of phosphorus at the Zn_1 level, which appeared to be associated with the extremely high phosphorus/zinc ratio⁷. The association of this ratio⁷ in plant and zinc deficiency were also reported by Millikan⁸. This suggests the hypothesis that a proper balance between phosphorus and zinc is necessary for normal growth as indicated by the maximum yield obtained at the P_2 Zn_1 treatment combination.

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33 fungal species associated with the leaves of *Spinacea oleracea* L. at various developmental stages of the leaves have been isolated. The free amino acids content, total sugars, the chlorophyll concentration, the dry matter production and the pH of the leaf have been assessed. A correlation between fungal population and the above factors has been established. The maximum population was recovered at the flowering stage. The spore germination studies have also been conducted in the leaf extracts and exudates and it was noticed that the spore germination of many fungi was enhanced by extracts and exudates of the leaf. An antagonistic effect between *Cercospora spinaceae*, an obligate parasite, and other commonly occurring isolates has been made and it was observed that the increasing concentration of the spores of other fungi individually decreased the germination of the above parasite.

Studies on Phyllosphere Fungi Part 6—Ecology of Leaf Surface Fungi of *Spinacea Oleracea* L.

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Introduction

Last¹ coined the term phyllosphere and further stated that like the rhizosphere, this region is also nutritionally very rich and offers a suitable niche for the colonization and multiplication of both, the saprophytes and parasites. Dickinson² recognized the term phylloplane for phyllosphere. In the present study, however, the author preferred to retain both the terms—phyllosphere and phylloplane to denote two distinct regions of the leaf analogous to rhizosphere and rhizoplane of the roots, as the two regions vary in nutrition level, thereby harbouring different types of fungi in the pattern as in the two above stated regions of the root. The fungal flora on living leaf surface has been worked out by many workers^{3–10}. In previous communications^{11–13}, the phyllosphere fungi of healthy and virus-infected plants in relation to the effect of plant extracts and MgCl₂ treatment on the leaf surface fungi had been studied. Earlier studies, however, had mostly been done without laying much emphasis on the ecology of fungi on leaf surface. The various factors involved in the colonization of leaf by fungi have not been worked out properly and need further investigation. The present paper gives an idea of the composition of leaf surface mycoflora of *Spinacea oleracea* and their succession at different stages of leaf growth, and the different factors, like amino acids, sugars of leaf extracts and exudates/

diffusates, and antagonisms between certain fungi in relation to leaf mycoflora, have been studied.

Materials and Method

Spinacea oleracea L., an important vegetable crop of the region, was selected for present study. It was raised in an experimental plot in the botanical garden in the campus of the University of Gorakhpur during December 1971. The first sampling of leaves for the assessment of fungi was completed when plants were 15 days old. The subsequent samplings were made at an interval of 25 days upto May, 1972 when the leaves were completely dead and even started to decompose.

The phyllosphere and phylloplane mycoflora were assessed according to the method used by Mishra and Srivastava¹⁰. The fungal population in the phyllosphere region of the leaf was calculated on per square cm. of leaf area. The leaf exudates were collected in accordance with the method suggested by Sol¹⁴. During last two samplings when almost all the leaves were dried, 10 leaves (thoroughly washed in sterilized distilled water) were put in 100 ml. of sterilized distilled water for 12 hours. The water, thus, obtained after filtration, was termed as leaf diffusate. The leaf extracts were prepared by crushing in a pestle mortar 2 g. fresh leaves of *S. oleracea* in 10 ml of 80 per cent ethanol, then squeezing, filtering, centrifuging and making up to 10 ml. by ethanol. The leaf exudates and extracts were analysed for the presence of free amino acids and total sugars by uni-

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directional paper chromatography and calorimetrically¹⁵⁻¹⁷.

The chlorophyll concentration of the leaf was also determined by paper chromatography using Whatman filter paper No. 24 and by a densitometer. The substitutes were prepared and the calculations of chlorophyll a and b were made¹⁷. The amino acids and sugars, chlorophyll concentration, dry weight of leaf and the pH of the extracts were determined from the part of the samples collected on each sampling date. The spore germination of certain phyllosphere fungi was studied in the leaf exudates/diffusates and extracts by the hanging drop method in cavity slides.

The spore germination of *Cercospora spinaceae* in presence of varying concentrations—50, 100, 150, 200, 250 and 300—of spores of 8 fungi, viz. *R. nigricans*, *A. flavus*, *A. fumigatus*, *P. chrysogenum*, *C. herbarum*, *C.*

epiphyllum, *A. tenuis*, and *Fusarium* sp., was studied separately. The suspensions of spores (taken from freshly sporulating cultures) of the above stated fungi and *Cercospora spinaceae* were so prepared in sterilized distilled water that each microscopic field contained approximately the ratio of *Cercospora* : other test fungus as 1:50, 1:100, 1:150, 1:200, 1:250 and 1:300. The studies were made by the hanging drop method in cavity slides.

Results

Isolation of Mycoflora : 33 fungal species (Table 1) were isolated from the leaf surface at six different stages of growth. Deuteromycetes and amongst them Aspergilli outnumbered throughout the present study. The maximum and minimum numbers of fungi were recorded during flowering and seedling stages respectively (Table 1).

TABLE 1—DISTRIBUTION OF FUNGI IN PHYLLOSHERE/PHYLLLOPLANE REGIONS OF *Spinacea Oleracea*

Fungal Species	1	2	3	4	5	6
<i>Absidia Spinosa</i>	+	+	+			
<i>Rhizopus nigricans</i>	++	+++	+/+	+/+	+/+	+
<i>Mucor hiemalis</i>		+	+	+		
<i>M. racemepsus</i>		+	+	+		
<i>Phoma</i> sp. 1			+/+	+/+	+/+	+/+
<i>Phoma</i> sp. 2				+	+	+/+
<i>Aspergillus aculeatus</i>	+	+	+	+	+	+
<i>A. flavus</i>	+/+	+/+	+/+	+/+	+/+/+	+/+/+
<i>A. fumigatus</i>	+	+	+/+	+/+	+	+/+
<i>A. niger</i>	+	+/+	+	+	+	+/+
<i>A. nidulans</i>						+
<i>A. terreus</i>	+	+	+	+	+/+	+/+
<i>A. tamaraii</i>			+			+/+
<i>A. sydowi</i>	+	+	+			
<i>Penicillium chrysogenum</i>	+	+	+	+	+/+	+/+
<i>P. notatum</i>		+	+			
<i>P. humicola</i>				+	+	
<i>P. terrestre</i>		+	+			
<i>Monilia geophila</i>	+	+				
<i>Cladosporium nerbarum</i>	+++++	+++++	+++++	+++++	+/+	
<i>C. epiphyllum</i>	+/+	+/+	+/+	+/+	++	
<i>C. lignorum</i>	+	+	+/+			
<i>Cercospora spinaceae</i>		-/+	+/+	-/+	-/+	
<i>Nigrospora sphaerica</i>				+	+	+
<i>Torula</i> sp.		+	+			+
<i>Alternaria tenuis</i>				+/+	+/+	+/+
<i>Fusarium nivale</i>	+/+	+	+	+	+	+
<i>Fusarium</i> sp.			+			
White sterile cols (W1)					+++++	+++++
White st. cols. (W2)	+/+	+/+	+/+	-/+		
Black st. cols					+	+/+
Grey st. cols.			+/+	+/+	+/+	+
Yellow st. cols.						+
No. of fungi	15/5	20/7	24/10	18/10	17/11	19/11
No. of cols/plate	/3	/6	/9	/5	/7	/13

+ = Present, ++ = Subdominant, +++ = Dominant, 1 = Seedling stage, 2 = Pre-flowering stage, 3 = flowering stage, 4 = senescence stage, 5 = harvest stage, 6 = Dead stage, — = Absence, Gaps = Also absence.

Rhizopus nigricans, *Aspergillus aculeatus*, *A. flavus*, *A. fumigatus*, *A. niger*, *Penicillium chrysogenum*, *Cladosporium epiphyllum*, *C. herbarum* and *Fusarium nivale* were found to be associated with the leaves of nearly all the stages. Other frequently occurring isolates were *Mucor racemosus*, *Phoma* sp. 1 and 2, *Aspergillus sydowi*, *Cladosporium lignorum*, *cercospora spinaceae*, *Torula* sp., *Nigrospora sphaerica*, *Alternaria tenuis* and white and grey sterile forms which were noticed in 3 or more stages. A few species, viz. *A. nidulans* and yellow sterile fungus, were noticed from the last and *Fusarium* sp. from third samples only (Table 1).

A. spinosa, *A. sydowi*, *Monilia geophila*, *C. lignorum* and white sterile fungus (W₂) were generally recorded upto senescent stages. *M. racemosus*, *P. notatum*, *P. humicola*, *P. terrestre* and *Fusarium* sp. were late appearing and short persisting. Species, like *Phoma* sp. 1 and 2, *Nigrospora sphaerica*, *A. tenuis*, white sterile fungus (W₁) and grey sterile form, appeared still late and persisted till the last. Other forms were of infrequent distribution (Table 1). The distribution of fungal species in phylloplane region exhibited a regular pattern. The number of fungi gradually increased with the age of the plants (Table 1).

Among 13 frequently occurring fungi except *A. aculeatus* all were recorded both in phyllosphere and phylloplane regions at one or the other stages of the plant growth. In phyllosphere region except for *Cladosporium* spp., the frequency (no. of colonies/plate) of frequent fungi generally exhibited an increasing tendency from seedling to preflowering stage. At flowering, in

majority of the species the frequency was further increased. Later, it decreased in a few cases or remained constant in others. For most of the fungi, the number of colonies/plate increased again from harvest to dead stage of the plant (Table 2). No regular pattern in the frequency of frequent fungi in the phylloplane region was noticed (Table 2).

The fungal population (fungi/sq. cm. of leaf area) in the phyllosphere region was comparatively low in seedling stage. It increased with the age of the plant till flowering and decreased gradually till the leaves became completely dead (Fig 1).

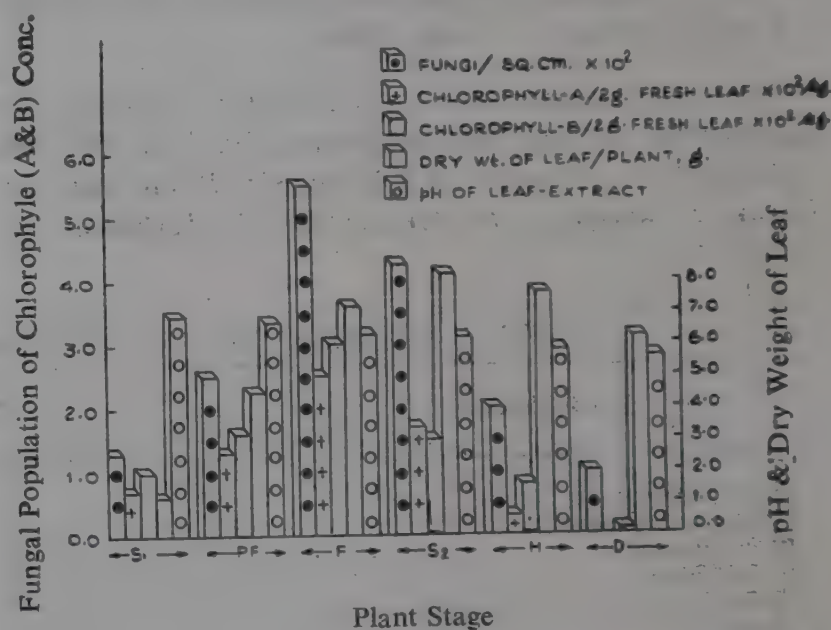


Fig. 1—Relation between Fungal Population and Age of Plant

TABLE 2—FREQUENCY OF DIFFERENT PHYLLOSHERE (COMMONLY OCCURRING) FUNGI
(Data based on 5 plates)

Fungal Species	Seedling	Pre-flowering	Flowering	Senescence	Harvest	Dead
	PS/PP	PS/PP	PS/PP	PS/PP	PS/PP	PS/PP
<i>Rhizopus nigricans</i>	3	4/1	3/2	2/2	2/3	3
<i>Phoma</i> sp. 1		2/1	2/2	2/2	3/2	4/3
<i>Aspergillus aculeatus</i>	1	2	4	3	2	1
<i>A. flavus</i>	2/1	3/4	4/3	4/3	3/3	5/5
<i>A. fumigatus</i>	1	1	3/2	2/1	2	3/2
<i>A. niger</i>	4	3/2	3	2	2	3/2
<i>A. terreus</i>	2	3	4	3	2/1	3/2
<i>Penicillium chrysogenum</i>	1	2	3	2	2/1	2/1
<i>Cladosporium herbarum</i>	5/5	5/5	5/5	5/5	5/5	
<i>C. epiphyllum</i>	5/4	5/4	5/5	4/4	3/3	
<i>Fusarium nivale</i>	1/2	2	3	3	2	2
White sterile cols. (W ₂)	3/1	3/2	3/3	—/2		
Grey sterile cols			2/2	3/3	4/4	4/4

PS—Phyllosphere region : PP—Phylloplane region.

Amino Acids and Sugars in the Leaf Extracts. Exudates/Diffusates : 8 amino acids (Table 3) were detected from the leaf extracts, exudates and diffusates at various sampling dates. Alanine and proline were generally present throughout the study. Glycine and methionine were noted at early stages, arginine and histidine at maturity and isoleucine and valine at later stages. Histidine and valine were only detected from the leaf extracts. The amount of amino acids (as μ g./2g. of fresh leaves) in leaf extracts exhibited the increasing tendency from seedling to the flowering stages. It decreased later till the leaves were dead. The maximum and minimum amounts were recorded in the leaves at flowering and senescence stages respectively. Similar was the trend of amino acids in the leaf exudates. These were present in leaf diffusates in traces only (Table 3).

6 sugars (ribose, rhamnose, sucrose, glucose, mannose and xylose) were chromatogrammed from the leaf-extracts and exudates of different samples (Table 4). Sucrose, glucose and xylose were occurring frequently in the extracts of all the stages of growth. Mannose was only present in leaf extract at the flowering stage. Rhamnose was first recorded from the samples taken at flowering stage and persisted till the end. The number

of sugars both in exudates/diffusates and extracts increased gradually from seedling till flowering when the highest number of sugars were detected. The quality of sugars in exudates/diffusates decreased later till the end (Table 4). The pattern obtained for the amount of total sugars was similar to that observed for the quality of the sugars (Table 4).

Chlorophyll Concentration and Dry Matter Production of Leaves : The concentration of chlorophylls (a) and (b) (expressed as μ g./2g. of fresh leaf) of leaf exhibited the following pattern : Both the chlorophylls increased from seedling to flowering stages. The maximum of the two was obtained at flowering stage. The sudden decrease of chlorophyll a and b was noted at harvest (Fig. 1). The data on dry matter production revealed that it was the lowest in the beginning, increased with age resulting in a maxima at senescence and later decreased till the end of the experiment (Fig. 1).

pH of the Leaf Extracts : The results of this experiment showed that the pH of the extracts was always acidic.

TABLE 3—DETECTION OF AMINO ACIDS FROM LEAF EXUDATES (E1)/DIFFUSATES (E*) AND EXTRACTS (E2) OF *Spinacea Oleracea* AT DIFFERENT TIME INTERVALS

Amino Acids	Seedling	Pre-flowering	Flowering	Senescence	Harvest	Dead
	E1/E2	E1/E2	E1/E2	E1/E2	E*/E2	E*/E2
Alanine	+/+	+/+	+/+	+/+	—/+	—/+
Arginine			+/+	—/+	—/+	
Glycine	+	+/+	+/+	—/+		
Histidine		—/+	—/+	—/+		
Iso-leucine			+/+	+/+	—/+	—/+
Methionine	+/+	+/+	+/+			
Proline	+/+	+/+	+/+	+/+	+/+	+/+
Valine					—/+	—/+
No. of amino acids	4/3	4/5	6/7	3/6	1/5	1/4
Amount (μ g./2g. fresh wt.)	0.5/310	25/675	105/1100	25/825	Traces/410	Traces/250

TABLE 4—DETECTION OF SUGARS IN THE LEAF EXUDATES (E1)/DIFFUSATES (E*) AND EXTRACTS (E2) OF *Spinacea Oleracea* AT DIFFERENT TIME INTERVALS

Sugars	Seedling	Pre-flowering	Flowering	Senescence	Harvest	Dead
	E1/E2	E1/E2	E1/E2	E1/E2	E*/E2	E*/E2
Ribose		—/+	+/+			
Rhamnose			+/+	+/+	—/+	—/+
Glucose	—/+	+/+	+/+	—/+	—/+	—/+
Sucrose	+/+	+/+	+/+	+/+	+/+	+/+
Mannose			—/+			
Xylose	+/+	+/+	+/+			
No. of sugars	2/3	3/4	5/6	2/4	1/4	1/4
Amount of Total Sugars (μ g./g. fresh wt.)	20/125	40/175	80/580	30/370	Traces/210	Traces/80

The lowest pH was found during flowering. pH during harvest and dead stages was near to neutral (Fig. 1).

Germination of Spores of Certain Fungal Isolates in the Leaf Extracts Exudates and Diffusates : The extracts and exudates/diffusates exerted a selective effect on various test fungi. The germination of spores of *A. flavus*, *C. herbarum* and *C. epiphyllum* was generally enhanced by the above three components of leaves of all the ages. The germination of spores of *R. nigricans* was also promoted by the exudates of most of the stages of the leaf. *Cercospora spinaceae* inhibited during seedling and preflowering stages was enhanced at the flowering and senescence stages in exudates and extracts, while that of *M. hiemalis*, *Phoma* sp. 1, *A. aculeatus*, *A. tamaritii*, *A. fumigatus*, *P. humicola* and *C. spinaceae* was

higher during flowering stage and that of *Fusarium* sp. was suppressed at all the stages (except that it was higher at the flowering stage in exudate) by exudates extracts and diffusates (Table 5).

Antagonism between Cercospora Spinaceae and Other Test Fungi : In this experiment the antagonistic effect of 8 phyllosphere fungi on *C. spinaceae* was studied separately. The data revealed that with increasing concentration of various test fungi generally decreased the percentage germination of conidia of *Cercospora spinaceae*. The highest germination of *Cercospora* was noticed in the lowest concentration (1: 50) of different fungi. *R. nigricans*, *A. tenuis* and *Fusarium* exerted a mild effect, where as, *A. flavus*, *P. chrysogenum* and *C. herbarum* decreased the germination upto a great extent. The

TABLE 5—GERMINATION(%) OF CERTAIN PHYLLOSHERE FUNGI IN LEAF EXUDATE, EXTRACT AND DIFFUSATE OF *Spinacea Oleracea*

Sampling	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>January 1, 1962</i>														
(i) Exudate	63	25	10	7	55	65	25	0.0	13	65	60	20	5	0.0
(ii) Extract	20	35	20	15	40	70	10	17	25	68	50	16	11	0.0
(iii) CW	60	50	40	25	55	60	45	40	45	55	50	65	30	36
<i>January 26, 1972</i>														
(i) Exudate	70	60	15	10	65	67	35	15	20	80	70	20	10	15
(ii) Extract	55	40	35	15	45	50	70	20	20	25	85	65	12	45
(iii) CW	65	50	30	30	60	50	40	50	55	60	85	37	37	38
<i>February 20, 1972</i>														
(i) Exudate	65	75	35	13	80	80	60	50	60	90	67	25	45	46
(ii) Extract	46	50	40	25	65	75	65	45	65	90	65	15	20	60
(iii) CW	70	55	35	30	61	63	40	42	45	60	40	90	45	40
<i>March 16, 1972</i>														
(i) Exudate	65	60	44	9	70	70	40	30	53	85	70	60	17	45
(ii) Extract	53	35	70	20	30	81	50	40	60	90	80	40	10	50
(iii) CW	50	55	35	40	63	60	40	45	50	60	65	90	90	40
<i>April 10, 1972</i>														
(i) Diffusate	50	20	40	40	40	65	33	15	30	75	65	90	10	10
(ii) Extract	60	35	50	45	65	75	40	30	35	80	75	90	17	35
(iii) CW	40	45	35	40	60	60	45	40	40	49	60	75	30	30
<i>May 4, 1972</i>														
(i) Diffusate	30	20	35	45	43	61	20	42	25	20	50	90	6	0.0
(ii) Extract	40	40	55	60	60	63	50	60	39	25	53	93	11	0.0
(iii) CW	40	50	35	40	60	60	45	40	40	40	45	80	20	30

1, *Rhizopus nigricans* ; 2, *Mucor hiemalis* ; 3, *Phoma*, sp. 1 ; 4, *Phoma* sp. 2 ; 5, *Aspergillus aculeatus* ; 6, *A. flavus* ; 7, *A. tamaritii* ; 8, *A. fumigatus* ; 9, *Pencillium humicola* ; 10, *Cladosporium epiphyllum* ; 11, *C. herbarum* ; 12, *Alternaria tenuis* ; 13, *Fusarium* sp.; 14, *Cercospora spinaceae* ; and CW—Control (distilled water).

remaining fungi had an intermediate effect on the spore germination of *C. spinaceae* (Table 6).

TABLE 6—GERMINATION* OF *Cercospora Spinaceae* IN VARYING CONCENTRATIONS OF CONIDIA OF OTHER FUNGI

Fungal Species	Concentration of <i>Cercospora</i> : Other Fungi					
	1:50	1:100	1:150	1:200	1:250	1:300
<i>Rhizopus nigricans</i>	40	35	37	32	20	15
<i>Aspergillus flavus</i>	26	20	15	10	0.0	0.0
<i>A. Fumigatus</i>	35	32	27	20	10	7
<i>Penicillium chrysogenum</i>	30	25	22	18	10	0.0
<i>Cladosporium epiphyllum</i>	35	30	26	20	17	25
<i>C. berbarum</i>	39	36	20	19	10	5
<i>Alternaria tenuis</i>	40	43	41	32	32	30
<i>Fusarium</i> sp	38	38	33	30	27	25

* Data representing in percentage and finalized on the basis of at least 1000 spare number of *Cercospora spinaceae*.

Discussion

The leaf was exposed to open atmosphere continuously subjected to air currents which carried the spores of various micro-organisms including fungi. The spore settled down and adhered to the leaf surfaces¹⁰. Consequently, the presence of many spores on the leaf surface of *Spinacea oleracea* is quite understandable. The germination of many of these adhered fungi on leaf surface is observed due to the exudation of various organic and inorganic substances from leaf itself^{6,7,9,14,18-23}. A good number of species have been isolated in high frequency from the leaf surface in the present study which may be due to the presence of different amino acids and sugars in the leaf exudates, diffusates and the extracts. The amino acids and sugars exuded from the leaves make the leaf surface nutritionally rich which permit better growth of fungi. Tandon and Bilgrami¹⁹ reported that the mixtures of amino acids had more favourable effect on certain fungi than individually. Moreover, the amino acids are known to break the dormancy of several fungal spores which presumably caused isolation of more fungi from the leaf surface in this study. Many fungi were commonly present at different stages of leaf which seemed to be related to some common amino acids and sugars in exudates and extracts of various stages (Tables 1, 3 and 4). Several fungi appeared early and persisted till the flowering, some showed a reverse pattern while a few appeared late and persisted for a short time, which may be ascribed to the exudation of certain specific nutrients during the respective stages (Tables 1, 3 & 4). This has further been confirmed with the spore germination studies in the extracts and exudates (Table 5). While working on phyllosphere mycoflora of certain crop plants, Tewari²⁵ sprayed the spores of *Puccinia graminis* (var. *tritici*) and other phyllosphere fungi in 1 : varying concentrations individually and in combination on healthy wheat leaves and observed the

decrease in the number of uredo- postules with increasing concentrations of other fungi. He suggested this decrease due to the antagonism. The possibility of such antagonism with the spores of *C. spinaceae* has been also observed in the present study. Unfortunately, this phenomenon has not been studied with the other fungi *in situ*. It would have given more clear idea of ecology of leaf surface fungi of *S. oleracea*. The work along these lines is in progress and will be published soon.

As evident from the present study, the role of pH of leaf extracts may also not be neglected. The better growth of fungi in acidic medium is well understood but such results are reported in soil and culture media. Nothing can be said regarding this aspect without carrying out such experiments with number of plant species.

The maximum fungal flora has been noticed at the time of flowering when the highest chlorophyll concentration and dry matter production by leaves have been observed (Fig. 1). At this stage possibly the highest photosynthetic activity resulted in the maximum leaf exudation and high amount of amino acids and sugars in leaf exudates and extracts supported the maximum fungi on the leaf surface. The spore germination studies with the extracts and exudates also supported this view^{6,7,9,10,14}. Comparatively, a higher fungal population at the harvest and dead stages may be related to the moribund nature of the leaf and the presence of dead mycelium on the leaf surface which resulted possibly increase in the nutrition status^{2,10-23}.

On the basis of their presence on phyllosphere and phylloplane regions at different stages of the leaf, the fungi isolated in the present study may be grouped into four categories, viz. (i) Transient fungi (*A. nidulans*, several species of *Penicillium*, *Monilia geophila*, *Fusarium* sp. and yellow sterile fungus) which were present on the leaf surface only as detectable propagules as they were recorded at only one or two of the different stages of the plant ; (ii) fungi of this category *A. spinosa*, *Mucor* spp., *A. aculeatus*, *A. sydowi*, *N. sphaerica* and *Torula* sp., which grew and multiplied on the leaf surface but could never penetrate the leaf tissues ; (iii) those which actively grew and sporulated and were able to parasitize the leaf tissues, their distribution being comparatively more continuous ; the majority of the fungi isolated belonged to this category ; and (iv) the fungi necessarily isolated from both phyllosphere and phylloplane regions. The latter can further be divided into two groups one group include species like *R. nigricans*, *A. flavus*, *A. niger*, *Cladosporium* spp., *C. spinaceae*, *Fusarium nivale*, white sterile fungus (W₂) and grey sterile form, which may live on green as well as moribund and dead leaves. The second group can only colonize moribund and dead leaves and may be treated as true saprophytes. *Phoma* sp. 2, *A. terreus*, *A. tamaritii*, *P. chrysogenum*, *A. tenuis*, white sterile fungus (W₁) and black sterile form may be grouped in this category.

The presence of sterile fungi during April and May, in the present investigation, may be possibly due to the

high temperature of the locality and low nutritional level²⁸.

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Polarographic behaviour of copper and zinc at dropping mercury electrode using methylamine as a supporting electrolyte has been studied. Both the metals gave well-defined diffusion-controlled irreversible waves in 0.5M methylamine + 0.1M sodium hydroxide + 0.01 per cent gelatin with half-wave potentials -0.36V and -1.38V (vs SCE) respectively. The values of diffusion current constant (I) have been evaluated. The linearity of diffusion current (i_d) with copper and zinc concentration provides a rapid and precise estimation of these elements and the system has been applied for the simultaneous determination of copper and zinc in low temperature Co-conversion catalyst.

A Polarographic Method of Simultaneous Determination of Copper and Zinc in Low Temperature CO-Conversion Shift Catalyst Using Methylamine as a Supporting Electrolyte

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Organic bases have long been used as a suitable complex-forming agent for copper and zinc, and the reduction of these metal complexes at the dropping mercury electrode has been studied by various workers¹⁻³. These complexing agents are important mainly because they are specific and selective, which the ordinary inorganic supporting electrolytes are not. Among the most important organic supporting electrolytes are pyridinium chloride⁴, EDTA with sodium hydroxide⁵, triethanolamine with sodium hydroxide⁶⁻⁹, glycine with potassium chloride¹⁰ and monoethanolamine with potassium chloride¹¹⁻¹². However, there is no reference in the literature about the application of methylamine as a base electrolyte in polarographic determination.

The present paper describes the results of a detailed investigation on the use of methylamine as the base electrolyte for the quantitative estimation of copper and zinc. It also deals with the simultaneous determination of copper and zinc in a low temperature CO-conversion shift catalyst. The difficulty in this simultaneous determination arises due to the fact that iron which is present in the catalyst undergoes reduction at the same potential as that of copper in most of the commonly used supporting electrolytes and thus interferes. In methylamine medium, copper produces a single well-defined cathodic wave and iron gets precipitated and hence is not reduced in this medium. Therefore, the direct analysis of

the catalyst for the simultaneous determination of copper and zinc was achieved without any interference from iron.

Experimental

Copper sulphate and zinc sulphate solutions were prepared from AnalaR reagents and their strengths were checked by the conventional procedures¹³. Methylamine (BDH) 25/30 per cent w/v in water was used for carrying out all the experiments. Gelatin (0.01 per cent) was used as a maximum suppressor.

Polarograms were recorded with a Radelkis (001) automatic recording polarograph using dropping mercury electrode and saturated calomel electrode. The drop time was maintained at 4.0 sec. with the open circuit and the product $m^{2/3} t^{1/6}$ was $1.32 \text{ mg.}^{2/3} \text{ sec.}^{1/6}$. Damping was kept constantly at 2. All experiments were performed at $25 \pm 1^\circ\text{C}$. The total volume of the solution (supporting electrolyte + metal salt solution) was 20 ml. and was deoxygenated by pure nitrogen before recording the polarogram.

Effect of Base Electrolyte Concentration : A number of polarograms were recorded by varying the methylamine concentration from 0.05 to 2M maintaining the pH and ionic strength constant. $E_{1/2}$ was shifted to more negative potentials with increasing concentration of methylamine in both the cases. The variation in base electrolyte concentration had no appreciable effect on the

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shape of the zinc polarograms but the copper polarograms became more irreversible with increasing concentration of methylamine. The results are recorded in Table 1.

TABLE 1—EFFECT OF METHYLAMINE CONCENTRATION ON COPPER AND ZINC POLAROGRAMS

Name of the Metal Ion	Metal Ion Conc., mM	Composition of the Indifferent Electrolytes	Conc. of the Ligand, M	Diffusion Current, μA	$E_{1/2}$ Volts vs SCE	Slope of $E_{d,e}$ vs $\log \frac{i}{i_d - i}$
Copper	0.4	0.025M Na_2HPO_4 + 0.01M NaOH + 0.01% gelatin.	0.05	1.95	—0.160	0.060
			0.1	1.80	—0.180	0.080
			0.2	1.80	—0.202	0.095
			0.3	1.72	—0.222	0.120
			0.4	1.65	—0.230	0.140
			0.5	1.50	—0.240	0.140
			0.8	1.50	—0.300	0.145
			1.0	1.32	—0.375	0.145
			1.5	1.25	—0.380	0.145
			2.0	1.25	—0.380	0.145
Zinc	1.2	0.025M Na_2OPO_4 + 0.01M NaOH + 0.01% gelatin	0.1	4.75	—1.300	0.060
			0.2	4.62	—1.318	0.080
			0.5	4.62	—1.330	0.090
			1.0	4.50	—1.340	0.090
			1.5	4.44	—1.345	0.085
			2.0	4.37	—1.345	0.085

Effect of Varying Metal Ion Concentration: Polarograms for various concentration of copper and zinc were recorded in 0.5M methylamine + 0.1M sodium hydroxide medium with 0.01 per cent gelatin as the maximum suppressor. The diffusion currents were calculated by extrapolation method. The data are given in Table 2.

TABLE 2—RELATION BETWEEN DIFFUSION CURRENT AND COPPER AND ZINC CONCENTRATION

(Base Electrolyte = 0.5M Methylamine + 0.1M Sodium Hydroxide* + 0.01% Gelatin)

Name of the Metal Ion	Metal Ion Conc., mM	Diffusion Current, μA	$I = \frac{i_d}{C_m^{2/3} t^{1/6}}$	Mean I
Copper	0.2	0.55	2.08	2.24
	0.4	1.19	2.25	
	0.8	2.38	2.25	
	1.2	3.60	2.27	
	1.5	4.44	2.24	
	2.0	6.20	2.34	
Zinc	0.2	0.75	2.84	2.94
	0.4	1.60	3.03	
	0.6	2.35	2.96	
	0.8	3.10	2.93	
	1.0	3.90	2.95	
	1.2	4.70	2.95	

Determination of Copper and Zinc in Methylamine Medium: Calibration curves were drawn by recording the polarograms of copper and zinc of various concentrations in 0.5M methylamine + 0.1M sodium hydroxide with 0.01 per cent gelatin as the maximum suppressor. For the actual analysis, 0.2-0.4g. of the finely powdered catalyst sample was digested with 25 ml. of *aqua regia* in a pyrex beaker until dissolution was complete. The solution was evaporated almost to dryness. The procedure was repeated with 10 ml. nitric acid (conc.). The beaker was cooled and the solid mass was redissolved in 50 ml. of hot distilled water. The solution was filtered into a 100 ml. volumetric flask and its volume made up to the mark. 1 ml. of this solution was pipetted out into a 25 ml. pyrex measuring cylinder. The pH of the solution was adjusted to 7.0 with calculated amount of dilute sodium hydroxide (0.5M) solution. Then 2 ml. of 5 M methylamine, 4 ml. of 0.5M sodium hydroxide and 2 ml. of 0.1 per cent gelatin were added. The volume of the solution was made up to 20 ml. and the polarogram was recorded under identical operative conditions. Copper and zinc were also estimated from the stock solution by conventional methods. The analysis of a typical catalyst sample by polarographic and conventional methods is shown in Table 3.

TABLE 3—DETERMINATION OF COPPER AND ZINC IN LOW TEMPERATURE CO-CONVERSION SHIFT CATALYST, %

Sample No.	By Proposed Method		By Conventional Method	
	CuO	ZnO	CuO	ZnO
1.	50.10	48.94	50.20	49.0
2.	50.32	49.0	50.10	49.10
3.	50.05	49.02	50.16	49.08
4.	50.22	49.10	50.08	49.04

Results and Discussion

Both copper and zinc produce a well-defined reversible single cathodic wave in 0.025M Na_2HPO_4 + NaOH buffer with 0.1 per cent gelatin as the maximum suppressor. Due to complex formation, the half wave potential values shift to more negative potentials with subsequent addition of the methylamine solution. Also i_d of the waves decreases with subsequent additions, of the methylamine. An analysis of the waves for the complexation (plot of $E_{d,e}$ vs $\log i/(i_d - i)$) was linear in all the cases except the theoretical slope, indicating that the reduction is irreversible since for any given polarogram the slope of plot of $\log i/(i_d - i)$ vs $E_{d,e}$ equals to 0.14V and 0.09V for Cu^{2+} and Zn^{2+} respec-

tively. The slope of the $\log(c)$ vs $E_{1/2}$ in the case of copper-methylamine complex was 0.07 and that of zinc-methylamine complex was 0.032 (Fig. 1). Since both copper and zinc produced single defined cathodic wave in methylamine medium it was assumed that both of them were reduced to metal leading to two electron change procedures. Under these circumstances, metal : ligand stoichiometry is 1:1 in the case of zinc and 1:2 in the case of copper. The plots of i_d as a function of square root of the height of mercury reservoir was found to be linear and passes through the origin, indicating that the reduction of Cu^{2+} and Zn^{2+} in methylamine medium is diffusion controlled.

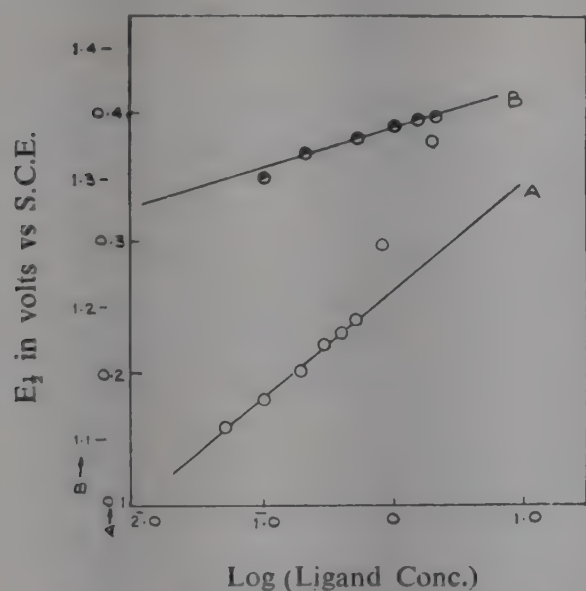


Fig. 1—Log (C) vs $E_{1/2}$ for Copper-Methyl Amine and Zinc Methyl Amine Complexes
A. Copper, B. Zinc

Conclusion

The linear variation of i_d with the concentration of Cu^{2+} and Zn^{2+} has contributed significantly to the use of the present data for analytical purposes and the calibration curves obtained almost identical conditions show that it is possible to estimate copper and zinc simultaneously in the base electrolyte mentioned in this study. The attainment of fairly constant values of diffusion current constant (I) and $i_d/\sqrt{h_{Hg}}$ justifies the diffusion controlled nature of the waves. The results

reported are reproducible and within limits of experimental errors. It may be pointed out that the method is comparable with other conventional procedures so far as its simplicity and precision are concerned. The possibility of separation and estimation of various multi-component systems in this medium are in progress. Indeed, it may be well claimed that the delineation of the operative conditions through a series of trial experiments, to introduce and also widen the scope of this base electrolyte in polarography, is perhaps the most noteworthy feature of this investigation.

Acknowledgements

The author thanks Prof. V. A. Altekar, Director, National Metallurgical Laboratory, Jamshedpur for providing facilities. He is also thankful to Dr. H. P. Bhattacharyya for encouragement and to the C.S.I.R. for financial assistance.

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Iron (III) forms a brown coloured chelate with salicylhydroxamic acid at pH 4.5-5.5, which is extractable with isoamyl alcohol. The coloured chelate formed can be directly measured spectrophotometrically at 450 nm. The system follows Beer's law at 450 nm over the sensitivity at 0.0127 $\mu\text{g Fe cm}^{-1}$ and a molar absorptivity of 4390, is found suitable for determination of iron present in China clay and other mineral specimens.

Extraction and Spectrophotometric Determination of Trace Amounts of Iron Present in China Clay

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Iron reacts with salicylhydroxamic acid forming brown coloured chelate at pH 2-6¹⁻³, which is extractable in isoamyl alcohol and the extract can be directly measured spectrophotometrically. This serves as a very rapid and efficient method for the determination of trace amounts of iron. The optimum conditions for this extraction and measurement have been determined and the method has been applied for determination of iron present in China-clay and other mineral specimens.

Experimental

Apparatus and Reagents: The absorbance measurements were made with a Beckman D.B. automatic recording spectrophotometer and for all pH measurements a Beckman pH-meter was used.

The reagent salicylhydroxamic acid was used after crystallization of the ordinary product several times (m.p. 167-168° C). All the reagents, including isoamyl alcohol, used were of analytical grade. Acetic acid—sodium acetate buffer of pH 4-5.5 was prepared in the usual way for all pH measurements.

Preparation of the Solutions: A stock solution of iron was prepared from AnalaR grade ferric alum. The iron solution was estimated volumetrically by potassium dichromate⁵ and EDTA⁶ method. 8.9 ppm. iron solution was prepared by proper dilution. A 0.01 M salicylhydroxamic acid solution was prepared by dissolving 0.153 g. of it in isoamyl alcohol.

Absorbance Curves: The absorbances of iron (III)-salicylhydroxamic acid chelate, extracted exhaustively from a solution having pH between 4.5 to 5.5 by the

above procedure, were measured at definite intervals between 350 and 650 nm against the reagent blank, which showed maximum absorption in the region lower than 340 nm. For the absorption measurements of the brown iron (III)-salicylhydroxamic acid chelate, the wave length 450 nm. was used throughout. The curve shows a peak at 450 nm. (Fig. 1).

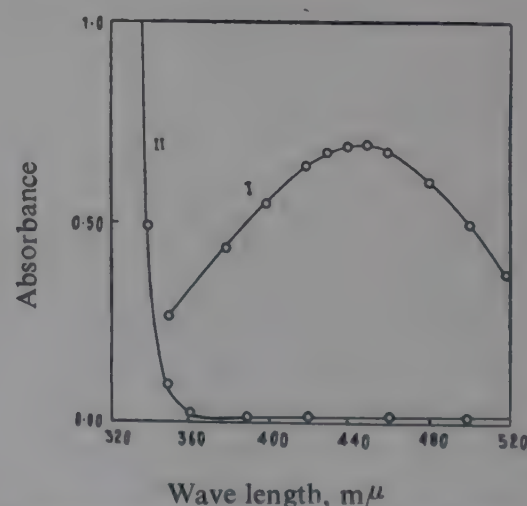


Fig. 1—Absorption Spectra of Brown Iron (III)-Salicyl Hydroxamic Acid Chelate

I—Spectra of the above Chelate extracted in Isoamyl Alcohol at pH 5.0

II—Spectra of Reagent Blank at pH 5.0 [(Fe. III) 8.9 ppm]

Effect of pH: A study of extraction of iron (III)-salicylhydroxamic acid complex in the pH range 1.25 to 6.0 was carried out. A complete extraction of iron (III)-salicylhydroxamate chelate was found to be possible between 4.5 and 5.5 pH in which range all the extractions were carried out. The percentage extraction of

iron (III)-salicylhydroxamic acid chelate at different pH values were determined (Fig. 2).

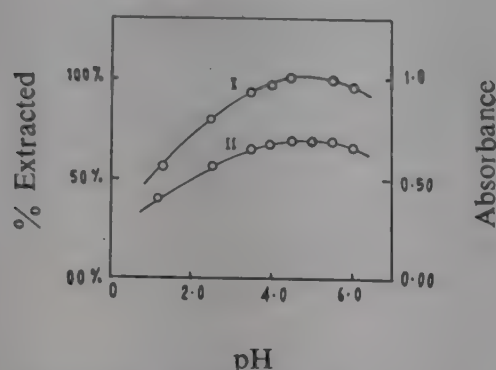


Fig. 2—Percentage Extraction (Curve I) and Absorbance (Curve II) of Iron (III)—Salicyl Hydroxamate Chelate Extract as Functions of pH.

Reagent Concentration: Salicylhydroxamic acid is highly soluble in methanol, ethanol, acetone, etc., but comparatively less soluble in higher alcohols, like isopropanol, isobutanol isoamylalcohol and hexanol. 0.01M concentration of salicylhydroxamic acid in isoamyl alcohol was found to be most suitable for extraction of iron. With lower the reagent concentration insufficient extraction of iron resulted, which was remedied by further extractions.

Beer's Law and Standard Curves: The iron (III)-salicylhydroxamic acid chelate system was found to obey Beer's law at 450 nm over the concentration range of 0.01 to 10 ppm. The sensitivity, $\log I_0/I = 0.001$, calculated as described by Sandell is $0.0127 \mu\text{g cm}^{-2}$ for iron (III) with a molar absorptivity of 4390.

Period of Extraction: The period of extraction was varied from 1 to 10 min. keeping other variables constant. 5 min. was found to be optimum.

Effect of Diverse Ions: In the presence of the following metal ions at pH 4.5 to 5.5, 4 ppm of iron could be determined after extraction with salicylhydroxamic acid in isoamyl alcohol without perceptible interference: Al^{3+} (100 ppm), Cu^{2+} (50 ppm), Co^{2+} (50 ppm), Cd^{2+} (100 ppm), Hg^{2+} (1000 ppm), Pb^{2+} (50 ppm), Mo^{6+} (50 ppm), Be^{2+} (100 ppm), Mg^{2+} (200 ppm), UO_2^{2+} (50 ppm), Ca^{2+} (200 ppm), Ni^{2+} (100 ppm), Ti^{4+} (50 ppm), Zn^{2+} (100 ppm), Sn^{2+} (50 ppm), Cr^{3+} (50 ppm), Mn^{2+} (50 ppm), Pd^{2+} (50 ppm), fluoride (10 ppm), oxalate (50 ppm), tartarate (20 ppm), phosphate (50 ppm), citrate (20 ppm), borate (20 ppm).

General Procedure: 10 ml. of iron solution containing 89 ppm of iron and 9 ml of acetic acid-sodium acetate buffer of pH 5.0 was taken in a 50 ml separatory funnel. After adding 10 ml of 0.01M salicylhydroxamic acid

solution in isoamyl alcohol, the mixture was shaken for 5 min. and allowed to stand, till the organic and the aqueous phases were separated. The aqueous phase was collected separately and pH of the solution was determined. Organic phase was collected after treatment with anhydrous sodium sulphate in a 10 ml volumetric flask and made upto the required volume with 0.01M salicylhydroxamic acid in isoamyl alcohol and absorbance was measured at 450 nm.

Determination of Iron in China Clay: The constituents of China clay are mainly silica, aluminium, manganese, iron, calcium, magnesium, etc. Powdered China clay (1 g.) was mixed with 5 g. of potassium bisulphate and taken in a boro-silicate test tube and the clay was fused in the usual way. The melt is leached with dilute hydrochloric acid, filtered, the filtrate and washings collected in a 50 ml of volumetric flask. The iron present in the China clay was measured in the usual way. It was calculated as follows:

$$\text{Iron in ppm} = \frac{100 \times \mu \text{ g of matching standard} \times \text{ml. of solvent phase}}{\text{ml. of aliquot}}$$

TABLE—IRON FOUND IN CHINA CLAY
(Katipara and Kendposi region of Singhbhum, Bihar)

Sample No.	Iron Present, ppm	Iron found by 1, 10-Phenanthroline Method ⁴ , ppm
S ₁	90	88
S ₂	180	168
S ₃	300	293
S ₄	450	441

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The treatment of a spent nickel hydrogenation catalyst with nitric acid and an incinerated material was carried out under varying conditions of acid concentration, temperature, duration and weight of material. The kinetic curves indicated higher rates for the incinerated product although the activation energies evaluated for both materials were generally the same, about 11.4. K cal. mole⁻¹. The recovery was found to be inversely proportional to the weight of extractable material and directly proportional to the initial acid concentration. A complete recovery of nickel was achieved by employing 5.1 N nitric acid at 80-90°C. However, a definite ratio should hold between the moles of acid to moles of nickel, which was 5:1 in case of the raw material, and 3:1 for the incinerated one.

Kinetics of Nitric Acid Recovery of Nickel from a Spent Hydrogenation Catalyst

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Introduction

Nickel takes part in many industrial and catalytic processes, particularly in producing edible hardened fatty oils. The activity of nickel decreases with time due to recrystallization or sintering and helps no more as a hydrogenating catalyst. This spent catalyst, is usually discarded when it contains an appreciable amount of finely divided nickel admixed with the partly hydrogenated oil. The reclaiming of nickel from this exhausted catalyst had been studied by many investigators¹⁻⁹, the usual treatment being the digestion with mineral acids, such as sulphuric, hydrochloric, and/or nitric^{2, 5, 7, 8} and occasionally organic acids, like formic^{4, 6, 7, 9} or acetic⁷⁻⁹. Sometimes the medium contained an organic solvent to help dissolving the oily residue as well^{2, 6, 8}. Thermal treatment has been referred to by Ramaswami¹ and Lal⁷.

Many of the studies had been directed towards the technical recovery of nickel, which are available in patent literature. Moreover, the effect of many factors concerning the optimum conditions of recovery is not clear. These factors are: temperature, concentration of acid, ratio of acid to exhaust catalyst and duration of digestion. Additional information could be gained when such factors are systematically investigated.

In the present study the effect of the various above-mentioned factors upon the nickel recovery from a

spent hydrogenating catalyst has been investigated. A parallel investigation was carried out on the same catalyst after being incinerated at 400°C.

Materials and Techniques

Materials: The starting material employed in this investigation was a spent hydrogenation catalyst obtained from the Salt and Soda Company, Alexandria. Its chemical analysis indicated the presence of 27.9 per cent nickel. Before taking the samples the material because of its non-homogeneity was thoroughly mixed.

The material was heated at 400°C for 3 hr, whereby the nickel content in the dry greyish-black product attained was 75 per cent. Upon dissolving the incinerated sample in nitric acid, an insoluble residue of 4.3 per cent was left, which on ignition at 1000°C gave a loss of only 1.3 per cent. These data indicated that the incinerated material was composed of low content of a carbonaceous residue together with nickel mainly in the form of its oxide. Ignition at 1000°C led to the loss of the carbonaceous matter in the form of oxides, meanwhile metallic nickel changed to the oxide.

Techniques: Nickel was determined chemically by the standard method¹⁰ by its precipitation with dimethylglyoxime.

Three series of experiments were performed on the

raw spent catalyst. Series 1 was carried out to study the effect of duration of heating at different temperatures (50-90°C) on the percent recovery. In these experiments 30 g. of the exhaust catalyst were digested for various durations with 100 ml. of 5.1 N nitric acid. In series 2, 10 g. of the spent catalyst and 100 ml. of nitric acid of varying concentrations, viz. between 7.7 and 1.4 N, were reacted at different temperatures for 5 hr. The experiments of series 3 were carried out by employing 100 ml. of different concentrations of nitric acid with varying weights of the exhaust catalyst ranging between 10 and 50 g. The reaction was continued for a uniform duration of 5 hr. at 50, 60, 70, 80 and 90°C.

For the incinerated material, two series of experiments were carried out. In series 1, 2 g. of the solid and 50 ml. of nitric acid of different concentrations were reacted and the recovery of nickel was followed for durations of 15 min. to 4 hr, at 30, 50, 70 and 90°C. However, only at 30°C the reaction was continued up to 25 hr. Series 2 was performed to investigate the effects of change in the volume of nitric acid (3.83 N) and weight of the dry incinerated material, and it was carried out at 50, 70, and 90°C for 5 hr. The weight of the solid ranged between 2 and 30 g.

In all cases, the experiments were carried out in glass stoppered reagent bottles immersed in a thermostatically adjusted water bath. Analytically pure concentrated nitric acid (15.4 M) was used, from which various dilutions were made in order to obtain the different concentrations.

Experimental Results

Recovery of Nickel from the Catalyst: Figs. 1-3 illustrate the effects of duration, temperature, acid

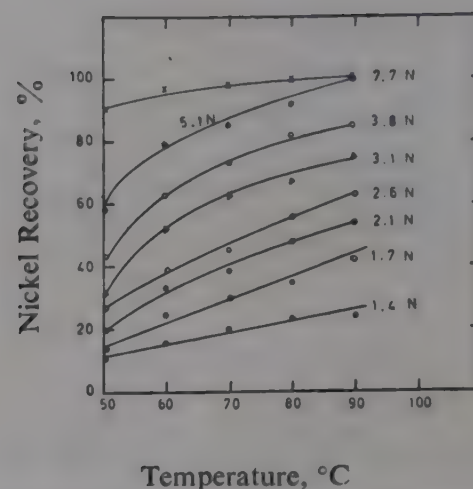


Fig 2—Temperature Dependence of Nickel Recovery from the Spent Catalyst at Various Acid Concentrations.

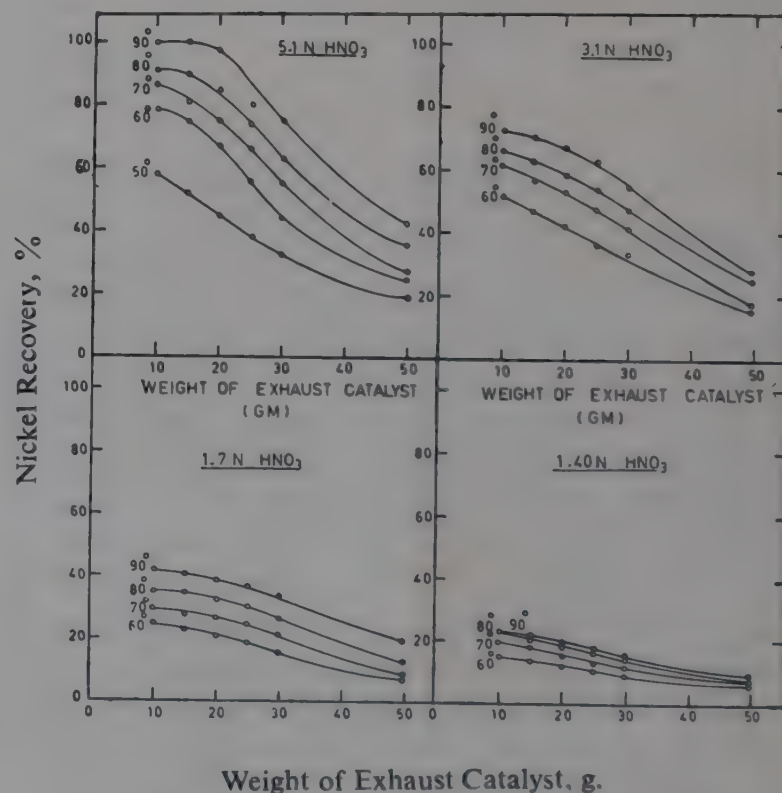


Fig 3—Dependence of Nickel Recovery on the Weight of Spent Catalyst.

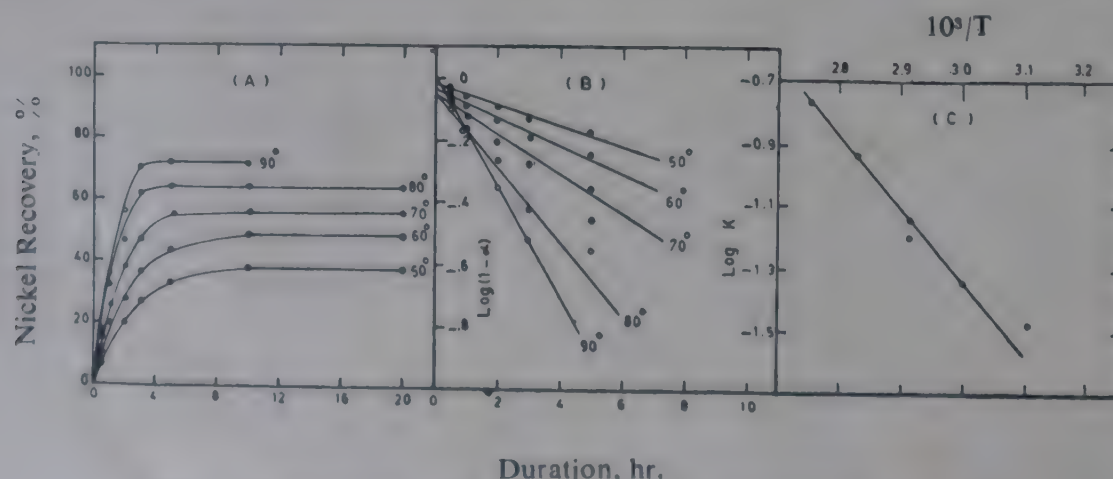


Fig. 1—Recovery of Nickel from the Raw Hydrogenation Catalyst
A—Kinetic Curves, B—First order Kinetic Plots, C—Arrhenius Plot.

concentration and weight of exhaust catalyst on the percent recovery of nickel. Upon using 5.1 N nitric acid, nickel recovery increased with increase in the duration of contact and attained limiting values which decreased at lower temperatures (Fig. 1). However, the reaction seemed to be slow as it needed 5 hr. at 90°C to reach the maximum, whereas it required 10 hours at 50 and 60°C. Meanwhile, nickel reclaimed at 90°C was only 72 per cent of the total nickel, which might be accounted for by the small ratio of nitric acid to weight of nickel ($R=3.4$) as discussed later. Applying the first order kinetic law to this reaction by plotting $\log(1-\alpha)$ vs time, yielded generally satisfactory straight lines [Fig. 1-B (α = fraction recovered of nickel)]. From an Arrhenius plot of the respective slopes (Fig. 1-C), the value of 11.7 K cal mole⁻¹ for the activation energy was evaluated.

An increase in the concentration of nitric acid produced profound effects on the recovery, even at 50°C (Fig. 2). The recovery increased almost linearly with raising the temperature although this effect was more appreciable at low acid concentrations. However, nickel was fully recovered only at high concentrations of the acid, viz. 7.7 and 5.1 N, at 90°C after 5 hr. These experiments indicated clearly the critical effect of the initial concentration of nitric acid employed in the extraction.

The effect of changing the weight of the material under acid extraction for the reaction carried out at specific acid concentrations was studied at five different temperatures (Fig. 3). The results revealed that the recovery of nickel was almost inversely proportional to the weight of the exhaust catalyst. The extent of decrease was more pronounced at the higher acid concentrations and temperatures. However, at a certain optimum weight of the exhaust catalyst, maximum recovery was attained which seemed unaffected by an additional decrease in weight (about 10-15 g.). Fig. 3 also indicates two more features. Nickel was reclaimed better at higher temperatures and concentrations, and the decrease in recovery with increase in weight was generally the same at all concentrations as is judged from the nearly parallel straight lines.

Recovery of Nickel from Incinerated Spent Catalyst: The effect of several factors viz. duration of contact with acid, temperature, weight of the incinerated material and the volume of used acid, on the recovery of nickel from the incinerated material was studied. The results are plotted in Figs. 4-6.

The dissolution of nickel took place quickly at all concentrations, the maximum reaching after 2 hr. The recovery of nickel attained limiting values dependent both on temperature and initial acid concentration; the complete recovery was attained at 90°C by employing an acid of 3.85 N. By plotting the kinetic curves in the first order kinetic law yielded some satisfactory straight lines [Figs. 5 (a-d)], from which the activation energies were evaluated by the Arrhenius plots (Fig. 5-e). The estimated activation energies were 9.7, 12.0, 11.3 and 11.7 K cal. mole⁻¹ for the extraction carried out at 3.85, 2.57, 1.95 and 1.4 N acids respectively.

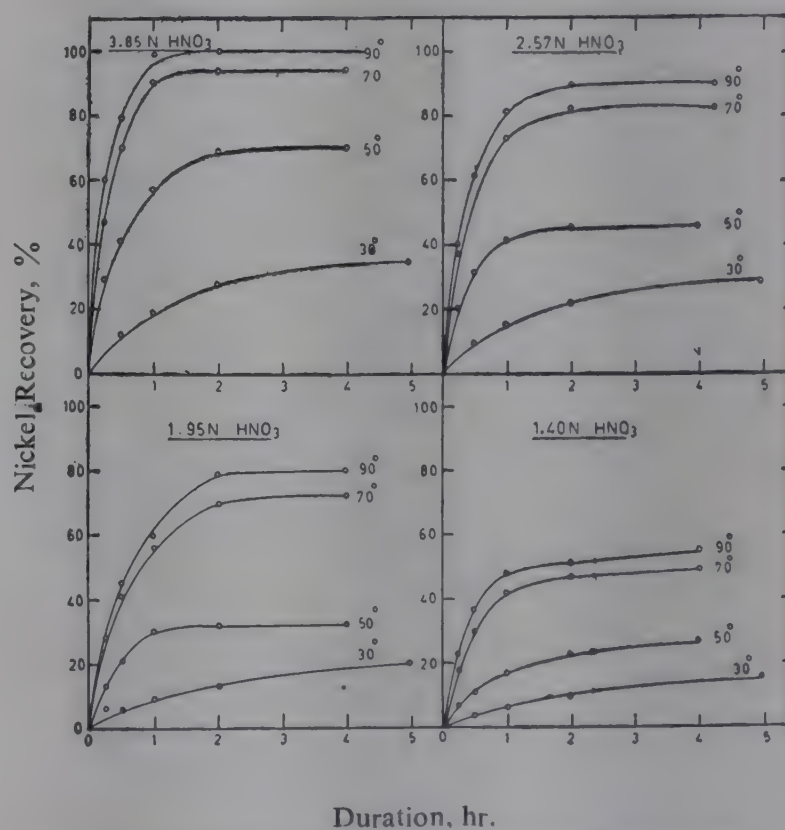


Fig 4—Kinetic Dissolution of Nickel from Incinerated Exhaust Catalyst

By changing the weight of the incinerated solid interesting results were obtained (Fig. 6). Thus, the percent recovery was perfectly inversely proportional to the increase in weight at the investigated temperatures. However, the same figure also indicated that, higher recoveries were attainable at higher temperatures and by using larger volumes of the same acid viz. 3.85 N, and that the decrease in recovery with increase in weight is more prominent at low temperatures.

An additional group of experiments was performed in which 15 and 30 ml. of either 15.4, 7.7 or 5.1 N nitric acid were added to 5 g. of the incinerated material, and the reaction was carried out at 90°C for 2 hr.

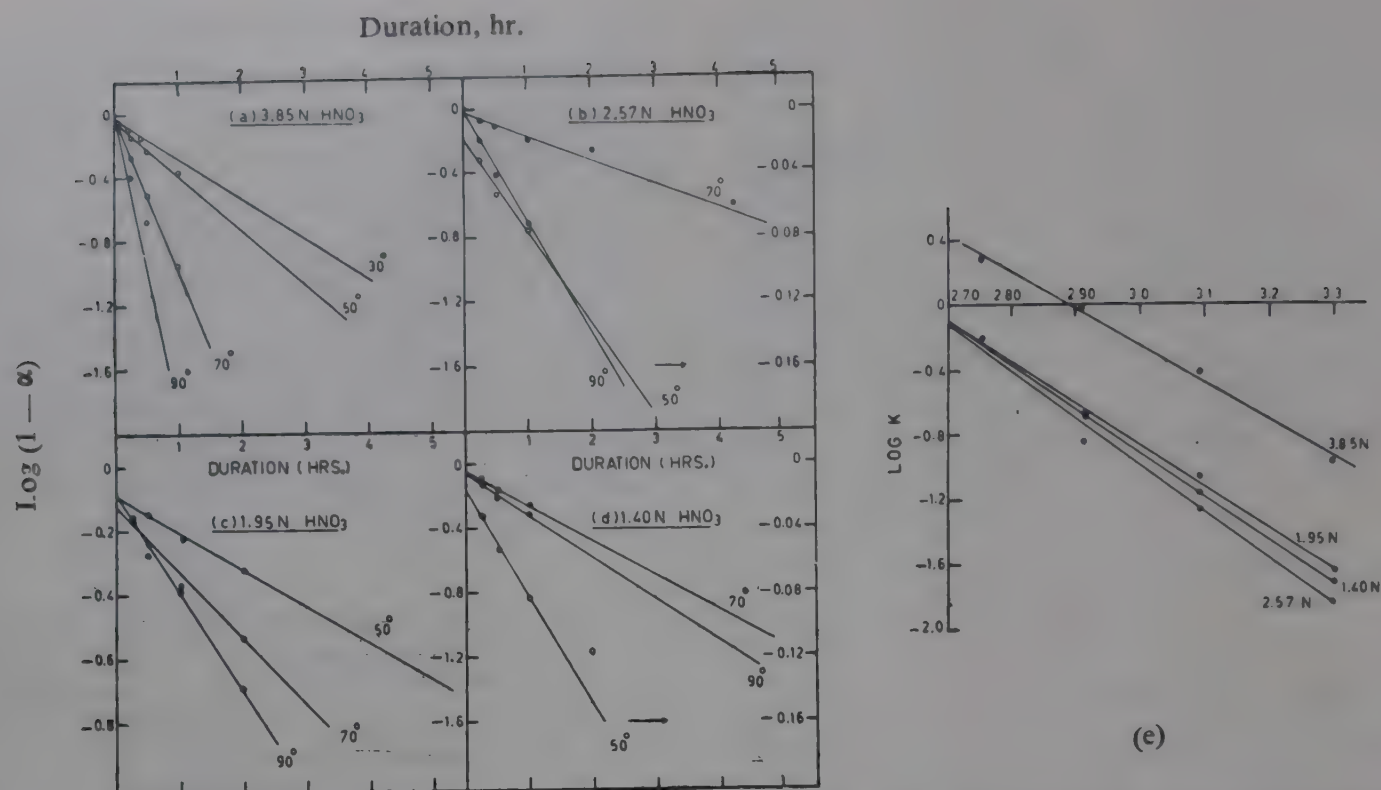


Fig 5—First Order Kinetic Plots (a — d) for the Recovery of Nickel from Incinerated Catalyst and the Respective Arrhenius Plots (e)

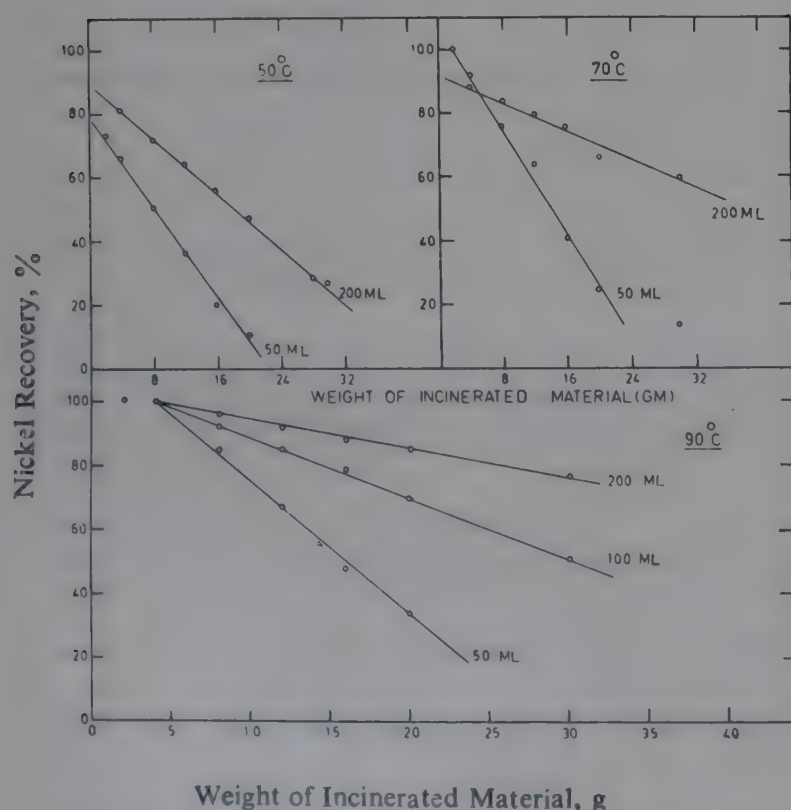


Fig 6—Dependence of Nickel Recovery on Weight of the Incinerated Exhaust Catalyst and on Volume of 3.85 N Acid

The obtained recoveries were found to be 84, 100; 83, 99; and 69 and 94 per cent respectively. These results showed that, in addition to the initial concentration of the acid, a certain volume should be present (cf. 15 ml. of 15.4 and 30 ml. of 7.7 N gave rise to 84 and 99 per cent recoveries respectively, although both of the two solutions contain the same amount of acid). Moreover, a complete recovery of nickel was

possible by employing nitric acid diluted to 1:1 or 1:2 (i.e. 7.7 and 5.1 N respectively).

Discussion

In the recovery of nickel from a nickel hydrogenation catalyst several factors are involved. These are temperature of reaction, duration of contact, initial concentration of acid and the amount of solid employed. Moreover, the ratio between the weight of extractable material to the amount of acid employed was found to be an important additional factor in determining the per cent recovery.

Thus, keeping all factors constant except temperature indicated a heat-dependent process, the activation energy of which amounted to about 11.0 K cal. mole⁻¹. This value was found to be almost the same when using either the raw spent hydrogenation catalyst or its respective incinerated product. However, it was slightly dependent on the initial acid concentration. This evaluated activation energy was close to the value of 12 K cal. mole⁻¹ reported by Dorofeeva and Kalichenko¹¹ for the activation energy of dissolution of pure nickel in 8 N nitric acid. In diffusion controlled dissolution reactions it was stated that the activation energy is about 4.5 K Cal. mole⁻¹. However, in the present chemical dissolution a higher value could be expected, especially in the partly hydrogenated oil medium.

Upon determining the isothermal recoveries of nickel, the rate of dissolution is given by $R=KS$

where S is the total surface area of the employed material (or alternatively its weight). The rate of dissolution also is equal to

$$D \frac{(C_s - C)}{\tau}$$

where D is the diffusion coefficient, C_s the concentration at the surface, C , the concentration in the bulk, and τ the residence time¹². When the solution was stirred occasionally the concentration gradient became negligible and the rate of dissolution proportional to the surface area and to the concentration of the acid. Hence,

$$R = D_s \frac{(C_s - C)}{\tau} = K.S.C. \quad (1)$$

This direct dependence is evident from Figs. 3 and 6, for the percent recovery as function of weight (or alternatively the surface area). In these plots, satisfactory rectilinear relationships are observed. However, the percent recovery of nickel was not ideally proportional to the initial acid concentration, except at low concentrations up to about 4 N, and/or at the low temperatures, viz. 30 and 50°C (Fig. 7).

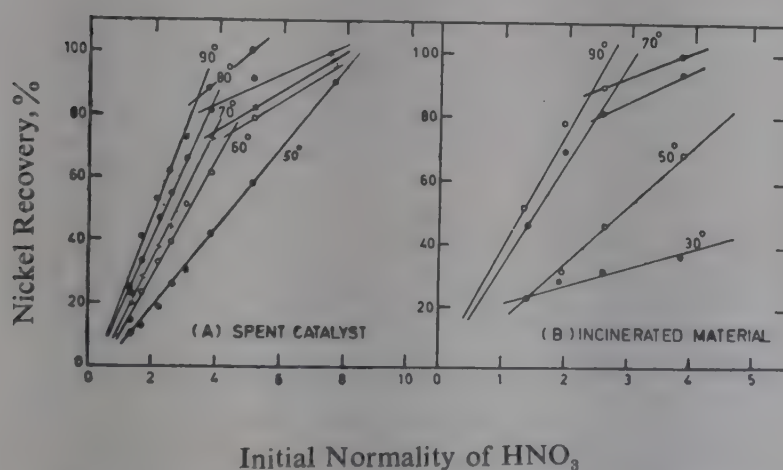


Fig. 7—Dependence of Nickel Recovery on Initial Normality of Nitric Acid for Spent Catalyst and Incinerated Product

A very important factor in attaining the maximum recovery was found to be the ratio of acid to nickel (in mole/mole) in the treated material (either the raw spent catalyst or the incinerated one). This effect is represented graphically in Figs. 8 and 9 for the former and latter materials respectively. These two plots indicate three points, viz. (1) for attaining the maximum recovery of nickel a certain excess of nitric acid should be present, for both of the raw spent catalyst and the incinerated product the ratio of acid to nickel should be around 6 (in mole/mole); nevertheless, the former was treated with a 5.1 N acid, and the latter

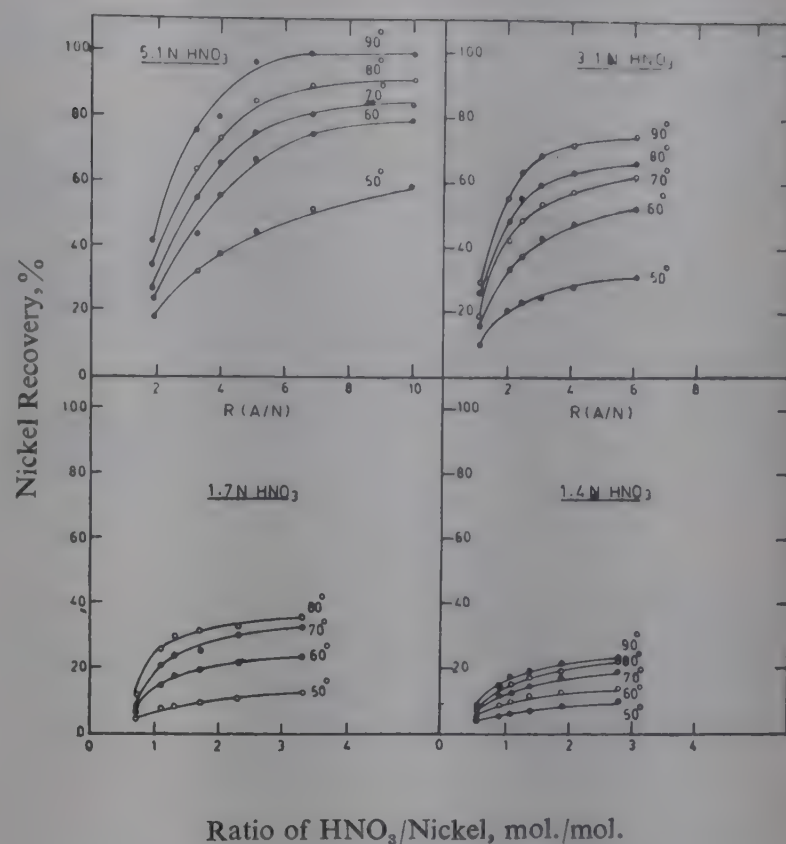


Fig. 8—Dependence of Nickel Recovery from Exhaust Catalyst on the Acid : Nickel Ratio (mol/mol)

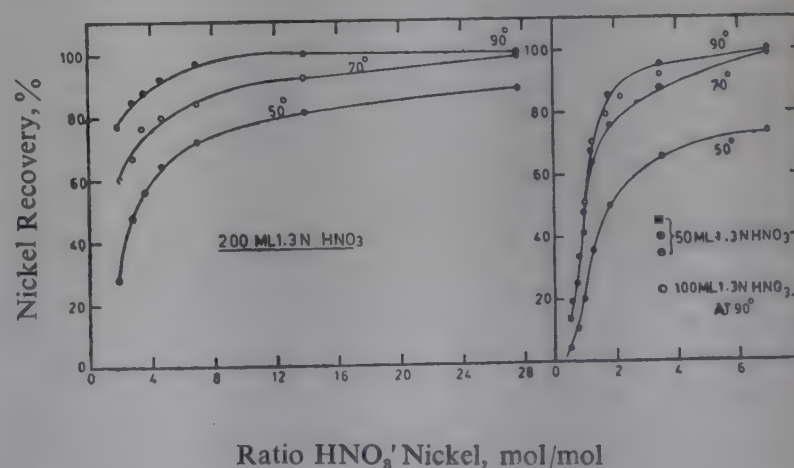


Fig. 9—Dependence of Nickel Recovery from the Incinerated Exhaust Catalyst on the Acid/Nickel Ratio (mol/mol.)

with 3.85 N acid; (2) the starting concentration of the acid is very important even though the acid: nickel ratio might be the same (Fig. 8); and (3) the volume of acid solution is not important as long as the ratio is fulfilled as observed from the recovery at 90°C (Fig. 9 B).

Nevertheless, in case of the incinerated material, and upon increasing the concentration of the initial acid to 5.1, 7.7 and 15.4N it was noticed that, a certain volume of the acid should be present (about 6 times the weight of solid). The same experiment also proved that an acid of 5.1 N could bring about com-

plete recovery of nickel at the low ratio of 3 between acid and nickel.

Conclusion

In conclusion, nickel could be quantitatively recovered from a spent hydrogenation catalyst or from the respective incinerated product by using nitric acid. The most suitable conditions could be an extraction carried out at 80 or 90°C, employing an acid of 5.1 N or higher, for 2-5 hr. The ratio between moles of employed acid to that of the present nickel should be about 5:1 for the raw spent catalyst and 3:1 in case of the incinerated material.

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In the present study silica gel has been modified by treatment with hydrofluoric acid and ammonia. In order to investigate the surface and structural changes in the modified support during thermal activation at successive temperatures (300-900°C), the physico-chemical and gas chromatographic measurements have been carried out. The gas-solid chromatographic behaviour of the modified support heated at different temperatures with a number of adsorbates, such as paraffins, olefines, aromatics, alcohols, esters, ethers, ketones and aldehydes, have been studied.

Gas Chromatographic Studies of Modified Silica Gel Heated to Different Temperatures*

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Porous silica beads were first used by Guillemin *et al*¹ as an adsorbent in gas-solid chromatography (GSC). The specific properties, such as polarity, adsorptive properties, etc., of this material were utilized in the complicated analytical problems and detailed investigations of salt modified porous silicas have been carried out recently²⁻⁷. A large number of supports with specific activities were made by modification of silica, alumina, etc. for a variety of gas chromatographic analyses^{2,8-12}.

A survey of literature reveals that in the past, Elmer *et al*¹³ had modified glass beads with ammonium fluoride for etching and widening pore dimension and the work was later extended by Sawyer *et al*¹⁴, who studied the effects of modification glass beads and silica gel at different temperatures and gave a tentative explanation of the mechanism from the elution properties of different aromatic compounds; only physical characteristics of the above supports were not studied by them.

The main interest of the present work is to correlate surface chemical nature of the support on different thermal treatments with gas chromatographic behaviour of the solutes, so that from the knowledge of the surface nature of the support it could be possible to predict qualitatively gas chromatographic properties of the solutes and *vice versa*.

In the present study, modifications have been carried out in the following two stages: (i) hydrofluoric acid

treatment and washing out excess of acid; and (ii) ammonia treatment with subsequent heating to 900°C.

Experimental

Silica gel of commercial variety was purified by acid washing and dried at 180°C for 7 hr. It was then treated with hydrofluoric acid in presence of sulphuric acid under specified conditions and washed with water till free from sulphate ions. The gel etched with hydrofluoric acid was treated with dilute ammonia solution and dried at 140°C for 7 hr. The dried product was activated at different temperatures at fixed time intervals.

The physical properties of the modified gel were studied as mentioned earlier¹⁰. The gas chromatographic studies were made with Aerograph Hy Fi 600D with flame ionization detector using copper columns of 5' × 1/8" (1.524 m × 0.003 m) dimension unless otherwise mentioned. Hydrogen used as a carrier gas, was of ultra-pure quality and obtained from Elhygen hydrogen generator (Model 9652). The columns were packed by the conventional method with support of uniform mesh size, i.e. 60-100 BSS for GSC. The standard support Chromosorb-P was procured from Applied Science Corporation, USA. Precision syringes (gas tight) were used for injecting 0.1 µl liquid samples. The retention data were reported on the average of triplicate runs and for the determination of retention indices corresponding normal hydrocarbons were injected before and after the compound. Retention indices of solutes in GSC were determined at 100°C.

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The 'modified support' hereafter signifies silica gel modified with hydrofluoric acid and 10 per cent ammonia and subsequently activated at various temperatures upto 900°C for 7 hours. Saturated hydrocarbons used were 2, 2, 3-trimethylpentane, 2, 3, 4-trimethylpentane, 2, 2, 5-trimethylhexane and cyclohexane and the olefins were hexene-2 and cyclohexene, while the aromatics were benzene and toluene. Alcohols, ketones, ethers and esters were methanol, ethanol, acetone, diethyl ether and ethyl acetate, and were represented as oxygenated compounds.

Results and Discussion

The physico-chemical properties of supports, modified under different conditions, along with relative retention of normal paraffins are given in Table 1. The relative retention is included in the physico-chemical studies (Table 1) since it has a direct bearing on the surface properties, such as surface area, pore dimension, etc.¹⁵. The GSC behaviour of the support for different solutes, (Table 2) indicated the physico-chemical changes

brought about by heating of the support at different temperatures.

Physico-chemical Properties : Ordinary silica gel is of hydrophilic nature but on hydrofluoric acid treatment gets converted to hydrophobic. This change-over had been ascertained due to transformation of Si-OH to Si-F, and as a result of this change, the pH of the gel dropped from 3.7 to 2.8. This has also been reported by other workers¹⁴ who explained it as an inductive effect of increased electronegativity of fluorine on conversion of Si-OH to Si-F in the gel. The pH of the above support remains constant on heating upto 900°C showing that residual fluoride which is bonded with silicon still persisted. On treatment of above support with ammonia and heating to 300°C, the pH remained 2.8 but the nature of the support was changed to hydrophilic indicating that chemical change had taken place, and most probably the fluoride attached to silicon had been replaced by OH from ammonium hydroxide with subsequent formation of NH₄F. This was further supported as the presence of NH₄F with silica lowers the pH of silica as

TABLE 1—PHYSICAL PROPERTIES OF THE STUDIED SUPPORTS AND GSC BEHAVIOUR OF NORMAL PARAFFINS AT 100°C

Supports	Colour	Physical Nature	pH	Packing Density, g./c. c.	Surface Area, m ² /g.	Relative Retention (non-adjusted)			
						n-Pentene=1.00			
						n-Hexane	n-Heptane	n-Octane	n-Nonane
Chromosorb-P	Pink	Hydrophilic	6.7	0.32	4.8	1.18	1.38	1.60	1.96
SiO ₂ -HF (300°C)	White	Hydrophobic	2.8	0.48	18	1.18	1.39	1.71	2.10
SiO ₂ -HF (350°C)	White	Hydrophobic	2.8	0.46	22	1.22	1.50	1.82	2.25
SiO ₂ -HF(900°C)	White	Hydrophobic	2.8	0.44	75	1.30	2.78	5.26	10.56
SiO ₂ -HF-10% NH ₃ (350°C, 7hr)	White	Hydrophilic	2.8	0.36	38	1.17	1.48	2.07	2.92
SiO ₂ -HF-10% NH ₃ (550°C, 7 hr)	White	Hydrophilic	3.0	0.38	47	1.39	1.90	2.96	5.09
SiO ₂ -QF-10% NH ₃ (750°C, 7 hr)	White	Hydrophilic	6.0	0.40	220	1.80	3.08	5.30	9.32
SiO ₂ -HF-10% NH ₃ (900°C, 7 hr)	White	Hydrophilic	6.4	0.41	345	1.85	3.20	6.18	11.25

TABLE 2—RETENTION INDICES OF DIFFERENT SOLUTES ON STUDIED SUPPORTS

Supports: Solute	Chromo- sorb-P	SiO ₂ -HF (300°C) 7 hr.	SiO ₂ -HF (350°C) 7 hr.	SiO ₂ -HF (900°C) 7 hr.	SiO ₂ -HF 10% NH ₃ (350°C) 7 hr.	SiO ₂ -HF 10% NH ₃ (550°C) 7hr.	SiO ₂ -HF 10% NH ₃ (750°C) 7 hr.	SiO ₂ -HF 10% NH ₃ (900°C) 7 hr.
2, 2, 4-Trimethylpentane	762	743	—	747	730	732	726	738
2, 3, 4-Trimethylpentane	762	743	—	—	764	758	761	749
2, 2, 5-Trimethylhexane	822	841	—	—	836	822	839	834
Cyclohexane	648	667	604	597	605	602	606	604
Hexene-2	794	700	—	647	700	711	683	659
Benzene	800	816	802	656	779	789	710	682
Cyclohexene	703	743	748	647	715	722	682	654
Toluene	942	981	—	—	920	904	819	813
Methyl Alcohol	916	did not elute	—	did not elute	983	908	763	782
Ethyl Alcohol	—	-do-	—	-do-	1045	938	895	912
Acetone	987	-do-	—	-do-	1243	949	852	964
Diethyl Ether	794	do-	—	-do-	1170	987	921	985
Ethyl Acetate	1032	-do-	—	-do-	—	957	—	1181

reported by Elmer¹³ *et al*, a similar observation was made by the present authors. The pH did not change appreciably upto 550°C. Further, an increase in temperature showed an increase in pH and at 750°C the pH of the support was noted to be 6.0 which reached to a maximum of 6.4 at 900°C. Therefore, it was inferred that there occurred a transformation in the modified support at high temperatures and thus it caused a rise in pH.

In support to above inference on the silica gel modified with hydrofluoric acid and ammonia, a regular increase in its surface area and bulk density had been noticed during the thermal activation upto 550°C and later it increased sharply at higher temperatures indicating a transformation which occurred in it at these temperatures. The relative retention of n-paraffins² on these modified supports and their bulk density also indicated that modification had little change in pore dimensions and surface area upto 550°C and later the pores were constricted and surface area increased considerably at higher temperatures i.e. 750 and 900°C. (Table 1).

Gas-Solid Chromatography: Kovats index system¹⁶ had been used for studying the physical and chemical changes in the modified support by elution characteristics of different types of solutes. In this study oven temperature was within $\pm 2^\circ\text{C}$ with subsequent variation of ± 4 index units.

Saturated hydrocarbons had been used for determination of surface properties since their bond formation with the support is related with support nature and thereby induced polarity to these solutes. Olefinic and aromatic compounds, which form bonds with hydroxyl groups of support², indicate the changes in hydroxyl groups concentration through their elution behaviour in the modified support at different activation temperatures. The total chemical changes brought about by modification in the support was observed from elution characteristics of oxygenated compounds because their elution is not only effected by hydroxyl groups of the support but by other polar groups as well².

The saturated hydrocarbons did not show any major change in their index values all along from 350°C to 900°C indicating that the activity of the modified support did not induce polarity to these solutes as to effect their elution (Table 2). Olefins produced an average change to ± 10 units on activation from 350 to 550°C. On further heating of the support from 750

to 900°C these values decreased by as much as 108 units. This indicated that hydroxyl groups, present in the modified support, had not been affected to any appreciable extent upto 550°C but thereafter it reduces to a marked level at 900°C, (Table 2). Retention indices of oxygenated compounds decreased upto 750°C but again rased at 900°C, (Table 2). The decrease in index values obtained for oxygenated compounds indicates that polar groups, such as fluoride and ammonium present in the modified support, went on decreasing in the course of transformation upto 750°C and on raising the temperature of activation to 900°C, new polar groups were formed in it as a result of which an increase in index values had been observed. The change of elution properties of these solutes from one temperature to other in the modified support gave an indication of its chemical transformation. The pH changes in the modified support at various temperatures also supported to this transformation because pH did not change much upto 550°C and thereafter a raise at 750°C which fixed at 900°C (Table 1). The exact reaction mechanism of the transformation taking place in the process of its modification could not be ascertained accurately. Physical methods of analysis, viz. X-ray and i.r., are required to know the exact state of different constituents during the transformation, which could not be done. It had been observed¹¹ that oxygenated compounds do not elute from silica gel treated with hydrofluoric acid alone, even when the temperature of activation was raised to 900°C whereas on ammoniation, these compounds are eluted even on activation at 350°C (Table 2). This showed that fluoride attached to silicon above did not help in their elution but on ammoniation this was achieved. Thus, it appeared from above inferences that silica gel modified with hydrofluoric acid and ammonia, behaved as NH_4F is coated on silica gel which masked its hydroxyl groups and helped in the elution of oxygenated compounds, which is otherwise not possible due to H—bonding with its hydroxyl groups². On increasing the activation temperature to 750°C and higher, it undergoes transformation due to solid state reaction which completed at 900°C and thereby the elution characteristics of different solutes were changed altogether from its activation at 350°C, (Table 2).

Therefore, from the analytical point of view, it may be concluded that the characteristic features of the modified support lies on the activation temperature also which effects the elution of solutes such as hydrocarbons, olefinic and oxygenated compounds and thus desired modifications can be done accordingly.

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A study on retention index of various types of solutes has been made at different temperatures in gas-solid chromatography. An explanation has been given for the retention index of different types of solutes being not linear to temperature on Porasil-D and silica gel, modified with hydrofluoric acid and ammonia, in contrast to gas-liquid chromatography and discussed its possibilities.

A Study on Retention Index at Different Temperatures on Sileaceous Supports in Gas-Solid Chromatography

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Introduction

The retention index in gas-liquid chromatography (GLC) is well-known¹. Its behaviour with temperature for different solutes has been studied² intensively for identification of different compounds in complex mixtures.³⁻⁸ The retention index of different solutes on various stationary phases has been utilized to characterize stationary phases⁹. Similarly, characteristics of different adsorbents were studied¹⁰ by coating them with squalane, a neutral phase, which reflected the effects of adsorbents through elution of different solutes. Vernon¹¹ mentioned in the study of aromatics on modified alumina that temperature coefficient of retention index of aromatics has negative values. The characterization of adsorbents might be possible by comparing the temperature coefficient of retention index of different solutes on it with non-specific adsorbent. Therefore, it was thought worth while to study the possibilities of characterization of adsorbents by temperature coefficient of retention index of different solutes in gas-solid chromatography (GSC). In the present study Porasil-D, a controlled pore silica gel¹² and a silica gel modified with hydrofluoric acid and ammonia had been chosen as representative adsorbents, since they are very common supports for modification and analysis of different types of compounds in GSC.

Experimental

Indigenous silica gel was purified as described earlier¹³ and treated further with hydrofluoric and

sulphuric acids mixture at 80°C under special conditions*. It was washed with distilled water till free from sulphate ion, followed by washing with 10 per cent v/v ammonia solution repeatedly to remove fluorine bonded with silicon¹⁴ and then oven-dried at 180°C for 4 hr. This product is henceforward marked SIHA in the text. Porasil-D was procured from Waters Associates Inc., USA. All reference compounds were procured from Philips Petroleum Co., USA. 'Precision' injection syringes were used to inject 0.2 c.c. of gas samples. The supports used were sieved properly into 60-100 mesh BSS, for SIHA and 100-150 mesh (BSS) for Porasil-D and packed into a 5" x $\frac{1}{8}$ " copper column by a conventional method. Beckman GC-2A with thermal conductivity detector was used in this work and the accuracy in temperature control was $\pm 1^\circ\text{C}$. The carrier gas used was nitrogen at 15 psi column inlet pressure. The solutes used were 2, 2, 4-trimethyl pentane, 2,3,4-trimethyl pentane, 2,2,5-trimethyl hexane, cyclohexane, methyl cyclohexane, cyclopentene, cyclohexane, hexene-2, heptene-2, benzene, toluene, cis-1, 2 dimethyl cyclohexane, trans-1, 2 dimethyl cyclohexane along with n-pentane to n-nonane saturated hydrocarbons. Two solutes of each type of compounds had been taken for comparison in the results. The retention time of each solute was taken in triplicate with the corresponding hydrocarbons for determining the retention index. The retention indices of certain compounds were checked by

* Due for coverage under a patent

their determination in a mixture and variations were marked by ± 4 units, which might be due to temperature fluctuations. The temperature range studied was from 70 to 190°C with rise of 30°C at each step. The temperatures higher than 190°C could not be studied because of the retention time being too close in the different types of compounds. The use of long columns for higher retention time was also not possible due to high pressure drop, because of finer particle size of the support.

Results and Discussion

The plot of retention index of the different types of solutes on Porasil-D and SIHA against temperature was found to be non-linear in GSC as compared to GLC² (Figs. 1 & 2). The most of the solutes studied did not vary much in their index values from 70 to 100°C on Porasil-D with the exception to cyclopentene, cyclohexene, benzene and toluene, which decreased considerably (Fig. 1). The decrease of the values of the latter varied from compound to compound. On rise of temperature to 130°C, the index values increased in all the them, except 2, 2,

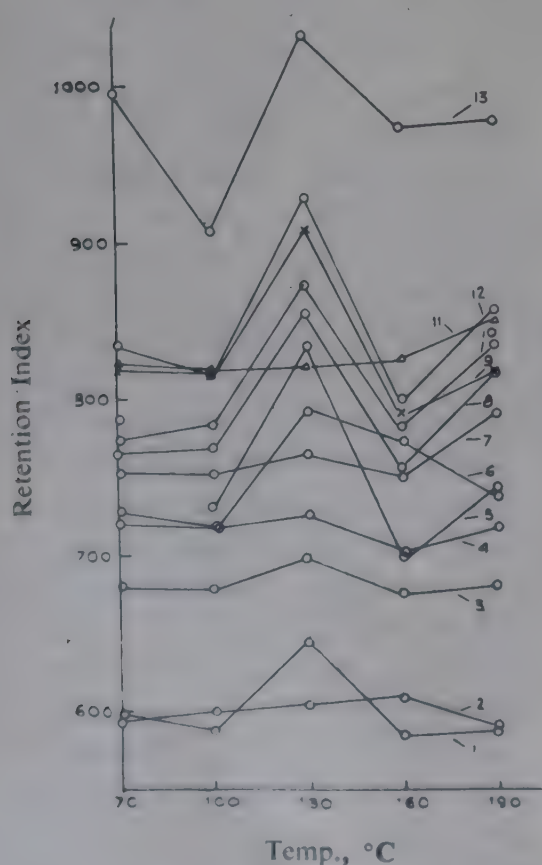


Fig. 1—Retention Index vs Temperature of Different Solutes on Porasil-D

Legend

1. Cyclopentene 2. Cyclohexane 3. Methyl Cyclohexane
4. 2,2,4, Trimethylpentane 5. Cyclohexene 6. Hexene-2
7. 2,2,4-Trimethylpentane 8. 1-Trans 2-Dimethyl Hexane
9. Heptene-2 10. 1-Cis 2 Dimethyl Hexane 11. 2,2,5-Trimethyl Hexane 12. Benzene 13. Toluene

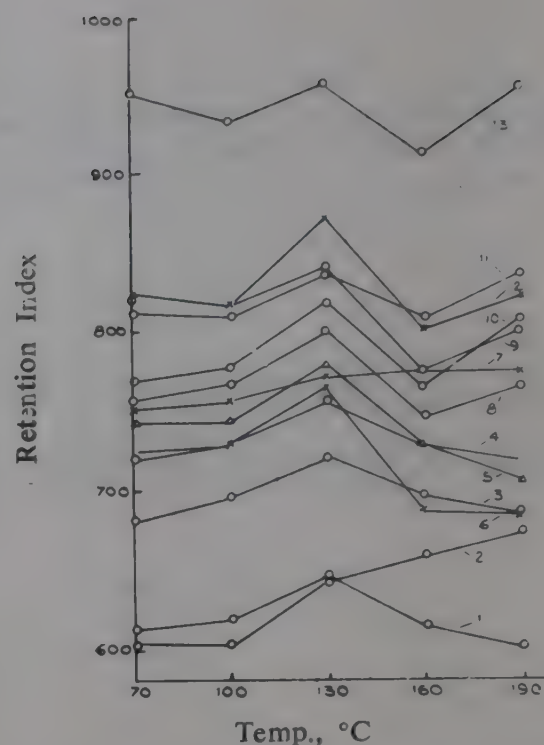


Fig. 2—Retention Index vs Temperature of Different Solutes on SIHA

4-trimethyl pentane, 2, 3, 4-trimethyl pentane, 2, 2, 5-trimethyl hexane and cyclohexane which did not change appreciably. The most of the values decreased at 160°C with exception to 2, 2, 5-trimethyl hexane and cyclohexane and again all of them increased (Fig. 1). It may be generalized from the above observation that 2, 2, 4-trimethyl pentane, 2, 3, 4-trimethyl pentane, 2, 2, 5-trimethyl hexane and cyclohexane, being non-specific type behave differently from other solutes at various temperatures. Whatever differences, marked in these cases are because of dehydroxylation of Porasil-D at different temperatures which affect the bonding¹⁵ between the solute and the support. Hexene-2 is the only compound with anomalous behaviour at 190°C, which could not be explained.

In SIHA also, there was not much variation in the index values upto 100°C in all solutes with an increasing tendency except benzene, toluene and heptene-2 (Fig. 2). Later in general, the index values increased from 100 to 130°C and then decreased at 160°C for different solutes leaving cyclohexane and 2, 3, 4-trimethyl pentane. The index of 2, 2, 4-trimethyl pentane, methyl cyclohexane, cyclopentene and cyclohexene decreased at 190°C, while with other solutes, except 2, 3, 4-trimethyl pentane and hexene-2, it did not change.

On summing up, it is seen that the behaviour of cyclohexane was different from that of methyl cyclohexene and also from those hexene-2 to heptene-2 on

both the supports, indicating the difference in their solute nature. This difference in their behaviour was not same on both the supports because of different support polarity. Porasil-D is a silica gel with controlled pore dimensions and surface area,¹² While SIHA is a chemically modified silica gel so it should have a different polarity¹⁶ than Porasil-D. This is further supported by comparing the behaviours of non-specific solutes as 2, 2, 4-trimethyl pentane, 2, 3, 4-trimethyl pentane, 2, 2, 5-trimethyl hexane on both the supports at different temperatures. It is seen that 2, 2, 4-trimethyl pentane had retention indices in the decreasing order, whereas 2, 3, 4-trimethyl pentane had them in a less decreasing order while 2, 2, 5-trimethyl hexane had become linear in Porasil-D within the temperature range. But in SIHA the nature of curve for 2, 2, 4-trimethyl pentane was opposite to 2, 2, 5-trimethyl hexane and 2, 3, 4-trimethyl pentane was linear between them. Cyclohexane behaved differently from methyl cyclohexane but the nature of their curves were not similar on both the supports. Specific solutes, like benzene and toluene, presented different curves from cyclopentene and cyclohexene in SIHA but their nature was the same as on Porasil-D. Therefore, these specific solutes, which form π bonds with the hydroxyl groups¹⁵ of these

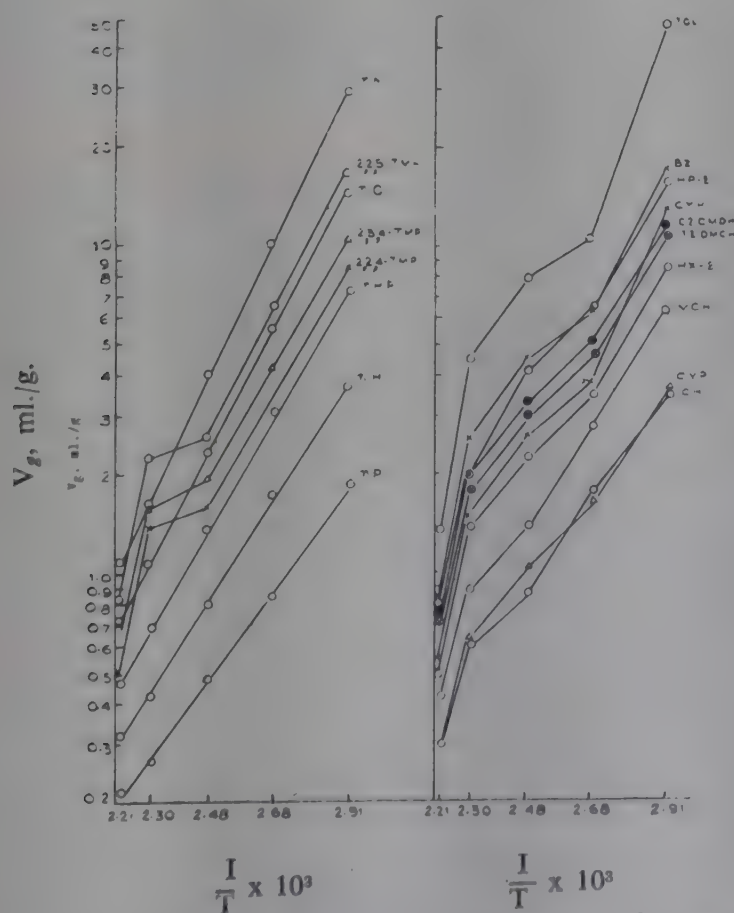


Fig. 3—Plot of Specific Retention Volume (V_g) vs $\frac{1}{T}$ on Porasil-D
[Abbreviations in Table 2]

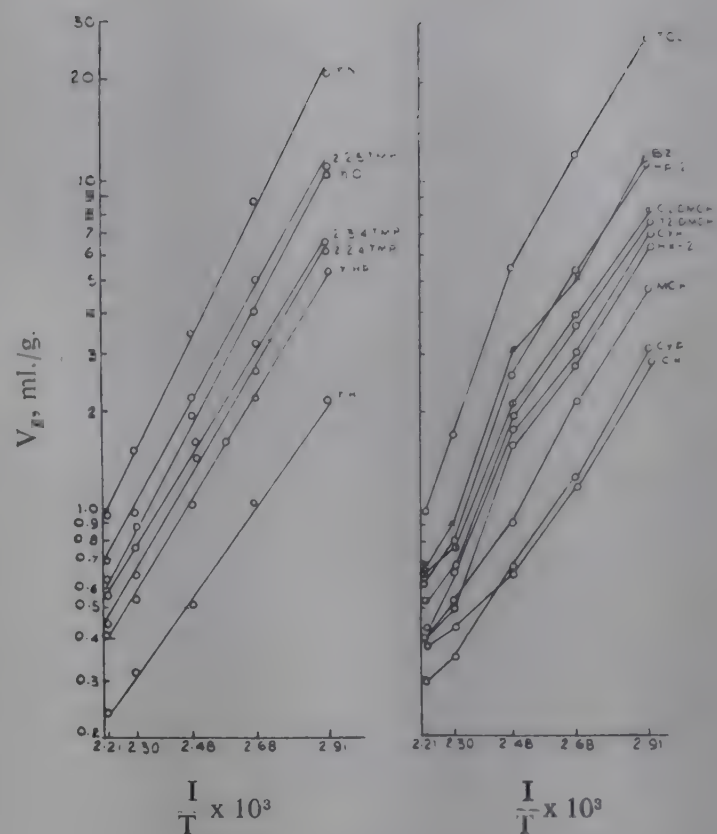


Fig. 4—Plot of Specific Retention Volume (V_g) vs $\frac{1}{T}$ on SIHA
[Abbreviations in Table 2]

supports along with non-specific solutes which form σ bonds with the same supports in GSC¹⁵, were also varying in their behaviour in these supports indicating the extent of differences in their polarity.

From the above observations, it can be inferred that the relation of retention index against temperature is not linear on the supports studied. Thus, the specific retention volumes (V_g) of different solutes were determined on these supports at various temperatures and log of them plotted against $1/T$ to determine support behaviour¹⁷. The plot of log V_g against $1/T$ of normal hydrocarbons is perfect linear with increase of slope for higher homologue in both the supports (Figs. 3 & 4). Normal hydrocarbons, being most non-reactive, remained unaffected during physical transformation of the support unless pore dimensions were changed¹⁵ which changed their specific retention volume, thus effecting slope value of the plot of log V_g against $1/T$. The branched hydrocarbons, like 2, 2, 4-trimethyl pentane, 2, 3, 4-trimethyl pentane, 2, 2, 5-trimethyl hexane, showed a break between 130 and 160°C in the plot of log V_g against $1/T$ in Porasil-D, Fig. 3. Since the rate of dehydroxylation calculated from TGA of silica-gel¹³ was not uniform (Table 1) and the polarity of the support was based on it¹⁵ so possibly Porasil-D induced polarity to these solutes at these temperatures, being itself more polar. In SIHA this was not observed for the

above solutes (Fig. 4). The difference in both the supports were marked in the study of retention index of different solutes as well. As regards the specific solutes, viz. aromatics, olefines and cycloolefines, the breaks in the slope of log Vg against 1/T at various temperatures have been observed and the variations in slope may be due to following possibilities.

Specific solutes formed π bonding with polar supports, like silica gel, etc.,¹⁵ which have active hydroxyl groups in them. The hydroxyl group present in the support was capable of forming equivalent bonds with specific solutes. In these cases, if the support did not change the active hydroxyl groups in it, the plot of log Vg against 1/T for specific solutes should be linear since the energy for π bonding changed linearly with temperature¹⁸. The normal paraffins gave perfect linear plots of log Vg vs 1/T in both the supports, but in the case of polar solutes the plots did have breaks in linearity, which clearly indicated the changes taking place in hydroxyl groups in these supports at various temperatures.

In support of the above inference, thermogravimetric analysis (TGA) for silica gel had also been done¹³. It was seen that weightloss in the silica gel was not uniform at various temperatures (Table 1). This weight-loss in silica gel within the studied temperature limit could only be due to the physisorbed water along with some temporary dehydroxylation of silica gel, which attained its position on cooling. This was confirmed experimentally also. Regarding SIHA, TGA was not done because it was essentially silica gel modified chemically to achieve low surface area and wide pore dimensions, otherwise SIHA is same as Porasil-D having different initial polarity due to modification.¹⁶ This observation has been pointed

Table 1—Rate of Decomposition of Silica Gel at Different Temperatures

Temperature °C	Percent De- composition of Total, w/w %	Rate of De- hydroxyla- tion g./°C
70	0.8	0.0114
100	5.4	0.1533
130	6.2	0.0266
160	7.0	0.0266
190	8.8	0.0600

Table—2-Symbols Used in Figures 3 and 4

Symbol	Compound
np	normal pentane
nH	normal heptane
nHp	normal heptane
nO	normal octane
nN	normal nonane
CH	cyclohexane
MCH	methylcyclohexane
2, 2, 4 TMP	2, 2, 4-trimethyl pentane
2, 3, 4 TMP	2, 3, 4-trimethyl pentane
2, 2, 5 TMH	2, 2, 5-trimethyl hexane
1T2 DMCH	1-trans 2, Dimethyl cyclo- hexane
1C2 DMCH	1-cis 2, Dimethyl cyclo- hexane
CyP	cyclopentene
CyH	cyclohexene
Hex—2	hexene-2
Hp—2	heptane-2
Bz	benzene
Tol	toluene

out earlier in this paper during the study of retention index against temperature and log Vg vs 1/T, for both the supports.

The above studies indicated that variation of slope of log Vg vs 1/T of specific solutes vary from one temperature to another due to variation of OH groups which vary their elution accordingly, differing from normal hydrocarbons which were not effected with it and have linear plot of log Vg vs. 1/T. Therefore, when elution of specific solutes were compared with the corresponding normal hydrocarbons for determination of retention index, resulted into its (retention index) non-linearity within the temperatures studied in both the supports. Thus, it may be concluded that the determination of temperature coefficient of retention index of different solutes in GSC can only be possible when the support showed stability by TGA or have linear relation of log Vg vs 1/T within the temperature to be studied. The support with high stability, as silanized silica gel, had linear relation of log Vg vs 1/T with different types of solutes in GSC¹⁹ and there it is quite possible to study temperature coefficient of retention index of different solutes.

This limitation will be difficult to overcome for most of the supports, therefore indirect method¹⁰ of GLC can be easily applied for qualitative indication of support activity.

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The physical properties, like surface area, pore volume and pore size distribution, of two series of ferric oxide-chromium oxide type CO-conversion catalysts have been determined before and after use. An attempt has been made to determine the effect of these properties of the used samples on activity.

Physical Properties of H-T. CO-Conversion Catalyst Before and After Use

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Introduction

Heterogeneous catalysis is a surface phenomena and the surface structures greatly influence the catalytic activity. During the process of activation of a catalyst the surface properties may undergo drastic change and in such cases the surface properties of the freshly prepared catalyst become less important. It is also not always possible to measure the surface properties of the reduced catalyst *in situ*. However, such properties can be conveniently measured by bringing the catalyst to the stable oxidized form. In practice, in an industrial converter when a catalyst is in use for a longer period (2-3 yr), depending on the plant conditions, some times it may become necessary to bring the catalyst back to the stable oxidized form and only under such a condition the samples can be taken out for study of physical properties in the laboratory. Such data can be of much help in predicting the performance of the catalyst.

Keeping this point in view, in the present work some studies were made with some H.T. CO-conversion catalysts discharged from the testing unit in the laboratory. In an earlier communication¹, the changes in physical properties and activity of a CO-conversion catalyst was studied with respect to the variation in mechanical activation period. It was felt necessary to see how these physical properties are reflected in the catalyst after use. Thus, in an extension to the previous work the physical properties have been studied for the two series of catalysts after

testing their activity. An attempt has been made to correlate these properties with the activity of the catalysts.

Experimental

The samples of series 3 and 4 (ferric oxide-chromium oxide) of the earlier work¹ were carefully oxidized in the bench scale unit after activity testing. A gas mixture containing 1-2 per cent oxygen in nitrogen was used for oxidation purpose. The samples in each series were serially named from A to G to represent different grinding periods.

The surface area, pore volume and pore size distribution of the discharged (after oxidation) samples were determined as before.¹

Results and Discussion

In the earlier work¹ it has been shown that the presence of chromium oxide imparts resistance to surface changes caused by ball milling. Also the role of chromium oxide has been established beyond doubt by different workers^{2, 3}. Hence, in the present study only two series of samples containing chromium oxide have been chosen.

H.T. CO-conversion catalyst on reduction is converted to Fe_3O_4 which on reoxidation is converted to $\gamma\text{-Fe}_2\text{O}_3$. There being similarity of structure in the catalyst before and after oxidation the surface structure may remain unchanged.

Uchida⁴, during his studies on iron oxide catalyst for CO-conversion reaction, has observed that when Fe_2O_3 (obtained after reaction) is oxidized back to ferric oxide at 500°C, the macro structure of ferric oxide becomes almost the same as it is in the case of Fe_2O_3 . Thus, it has been assumed in the present study that the surface structure remains almost unaltered before and after oxidation.

The pore volume and pore size distribution of the discharged samples are given in Table 1. Side by side the data for the fresh samples are also given for comparison. It can be seen that in almost all the discharged samples the pore volume is less than the corresponding fresh sample. The percentage of small pores decrease and that of the bigger pores increase. So it appears that during reduction of the catalyst bigger pores are created by the collapse of the small pore wells. The loss of small pores is also reflected in a lowering of the surface area. Uchida⁴ observed that the change, ferric oxide to Fe_2O_3 is accompanied by an increase in the size of pores. The present observation is similar to that of Uchida. From a comparison of the pore size distribution data for different samples no regular trend could be observed. For the fresh samples, the pore volume decreased up to 75 hr. of grinding and thereafter became steady. But in the discharged samples the pore volume became almost steady for all samples except A.

The surface area of the fresh and discharged samples is shown in Fig. 1. It has been pointed out earlier¹ that for the fresh samples the surface area does not indicate a specific trend with period of grinding and instead periodical changes occur similar to the observation of Naiser *et al*⁵.

In the present case for the discharged samples also a similar type of periodic change occurs. However, it is to be seen that the maximum surface area for the discharged samples of series 3 and 4 occurs corresponding to 100 and 50 hours of grinding. A comparison of activity data, reported earlier¹, and the

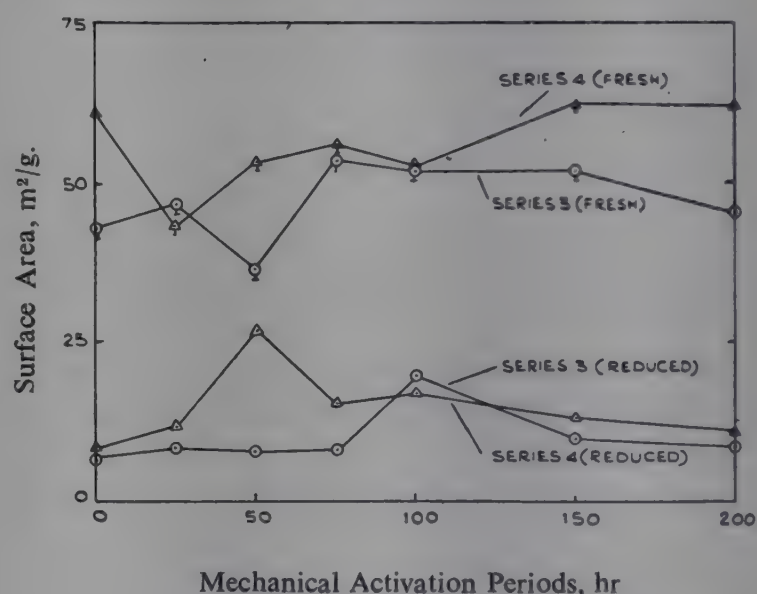


Fig. 1—Surface Area of Fresh and Reduced Samples.

TABLE 1—PORE VOLUME AND PORE SIZE DISTRIBUTION OF FRESH AND DISCHARGED SAMPLES

Sample	Fresh				Discharged			
	Pore Vol., c.c./g.	Pore Size Distribution, % Vol.			Pore Vol., c.c./g.	Pore Size Distribution, % Vol.		
		4-300A°	300-500A°	500-75000A°		4-300A°	300-500A°	500-75000A°
3 A	0.2056	71.3	14.1	14.6	0.2036	8.7	21.5	69.8
3 B	0.1506	95.4	2.3	2.3	0.1460	62.9	30.6	6.5
3 C	0.1422	98.2	0.4	1.4	0.1443	90.8	3.8	5.4
3 D	0.1430	74.9	3.9	21.2	0.1454	66.5	7.1	26.4
3 E	0.1462	85.4	4.2	10.4	0.1438	79.1	7.2	13.7
3 F	0.1446	85.7	3.8	10.5	0.1424	75.2	9.1	15.7
3 G	0.1458	79.4	5.0	15.6	0.1451	65.8	15.3	18.9
4 A	0.2921	54.0	19.4	26.6	0.2649	46.3	22.6	31.1
4 B	0.1758	77.0	11.2	11.8	0.1600	54.1	21.9	24.0
4 C	0.1600	91.4	5.1	3.5	0.1562	78.1	8.5	13.4
4 D	0.1556	90.2	7.4	2.4	0.1516	82.2	8.8	9.0
4 E	0.1580	84.3	11.6	4.1	0.1502	73.5	9.8	16.7
4 F	0.1552	87.7	7.8	4.5	0.1525	82.3	8.5	9.2
4 G	0.1558	82.9	6.1	11.0	0.1498	66.0	15.7	18.3

surface area of the discharged samples reveals some interesting results, and one such case is shown in Fig. 2. Here, the maximum activity corresponds to the maximum surface area of the discharged sample for both the series. But no such relation could be seen with the fresh samples. Puri *et al*³ in their

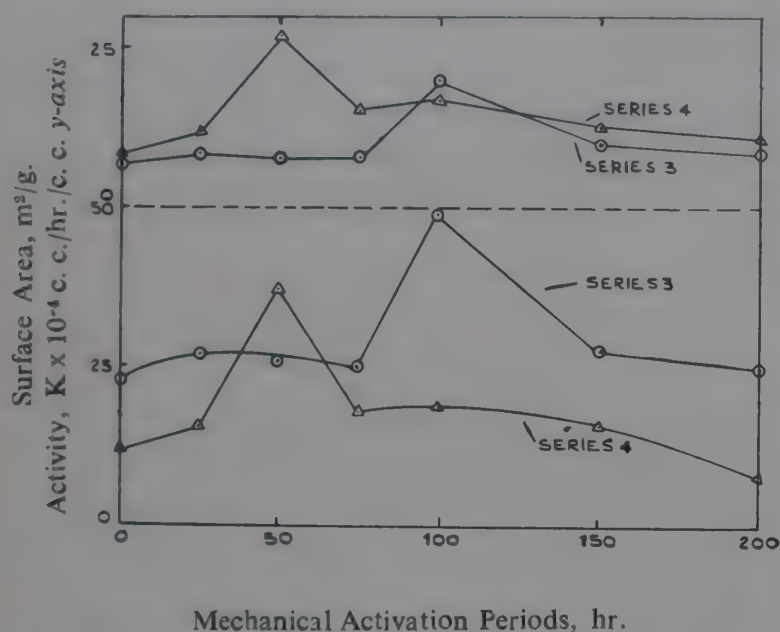


Fig. 2—Activity and Surface Area of Reduced Samples

study on heat treatment of iron oxide-chromium oxide catalyst, have reported a linear relationship between surface area of discharged catalyst and catalytic activity. In the present case no such relationship could be obtained. This may be due to the fact that during the preparation of the catalyst, the different period of ball milling bring about disintegration and agglomeration of particles in a monotonous way and this in turn is reflected in the discharged samples.

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Considerable weathering of Amjhor pyrites occurred after 7 weeks with size disintegration. A loss of over 4 per cent of sulphur value was observed.

Weathering of Amjhore Pyrites

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There is a significant deposit of pyrites mineral at Amjhore in the Sahabad district of Bihar. A 30 ft. thick seam has been proven to contain about 80 million tonnes.¹ This pyrite is now being utilized in the 400 te/day sulphuric acid plant, and has also been considered for another 880 te/day plant at Sindri, for which it has to be transported to about 200 miles.

This deposit of pyrites is too much susceptible to weathering and has the characteristics to decompose by exposure to atmosphere. It readily changes by oxidation to iron sulphate or to hydrated iron oxide, i.e., limonite, with sulphuric acid setting free. Even after storage for 3-4 days, it gets covered by a visibly white incrustation, particularly in the rainy season when it is more prone to weathering. A lot of sulphur loss occurs by its oxidation and leaching by the formation of ferrous sulphate and sulphuric acid. A study of the quality of this pyrites, both freshly mined and after its transportation to Sindri, has been made. This has particularly been done for utilization of this deposit at Sindri's sulphuric acid plant when considerable size reduction of the ore was expected in transit accompanied by loss of sulphur. Moreover, stocking of this ore in view of its highly weathering nature poses another problem which if proper care is not taken might lead to the formation of hard cake.

Experimental

Studies were made on the size and chemical analyses of the pyrites. The first part of the experiment

was done at Amjhore, when a batch of 18 te of freshly mined ores was taken for screen analysis. Immediately after screen analysis, an overall sample was prepared on the spot and kept in a sealed container for laboratory evaluation for sulphur. The screened sample was sent to Sindri in a closed wagon for repeating the same test.

Results and Discussion

Size analysis of the pyrites, carried out at Amjhore and at Sindri after a lapse of 7 weeks, is given in Fig. 1.

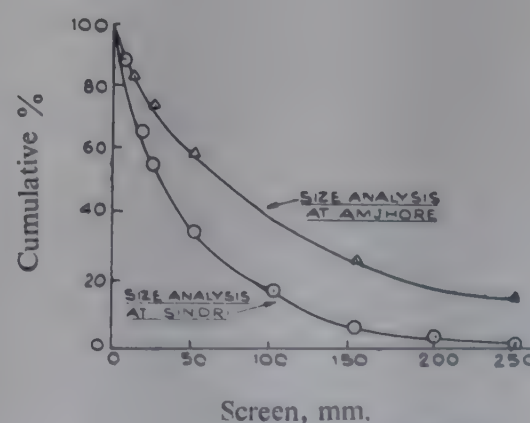


Fig. 1—Screen Analysis of Pyrites

The total sulphur in the freshly mined pyrites was 25.9 per cent but the same had reduced to 24.8%

when sampled and analysed at Sindri. Thus, a reduction of 1.1 per cent of sulphur in the overall ore (normal range of sulphur 23-27 per cent) was noticed in 7 weeks' interval. This loss in terms of sulphur value amounts to about 4 per cent. A detailed chemical analysis of the pyrites after collection at Sindri is given in Table 1.

Table 1—Chemical Analysis of the Pyrites

Constituents	%
Sulphide Sulphur	24.00
Sulphate Sulphur	0.80

Total Sulphur	24.80
Total Iron	23.00
Silica	32.70
Alumina	12.75
Lime	1.26
Magnesia	0.56
Carbon	2.50
Copper	0.005
Phosphorus	traces

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A kinetic study of the reaction of steam with calcium sulphide, obtained by the reduction of gypsum with coal, has been carried out at different temperatures below 900°C. Sulphur is liberated in the form of both hydrogen sulphide and sulphur dioxide gases.

Studies on the Reaction of Steam on Reduced Gypsum

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Introduction

In an earlier work, it has been shown that gypsum can be successfully reduced to calcium sulphide¹, followed by liberation of hydrogen sulphide from the reduced mass by carbon dioxide². The economic consideration of the problem has been analysed by U.S.B.M.³, as in the process considerable heat is lost in cooling the reduced mass. In another study by Farooque et al⁴, a two-stage method was investigated involving reduction of gypsum to calcium sulphide, followed by formation of hydrogen sulphide by the action of steam in the other part of the reaction tube. This method⁴ seems attractive since the reaction takes place at the reduction temperature with steam which is relatively inexpensive. In the present work, only the part covering the reaction of reduced gypsum with steam has been studied in details.

Experimental

Natural gypsum reduced by bituminous coal was used in all the experiments. Initially reduced and powdered gypsum was taken in a boat and introduced into the tube furnace. Steam, generated in a flask and carried by nitrogen to prevent condensation, was passed through the tube at a sufficiently good rate. The temperature was gradually raised and kept constant for $\frac{1}{2}$ hour at each of the following temperatures: 400, 500, 600 and 700°C. At 700°C, a very small quantity of hydrogen sulphide evolved, which was detected by absorbing the gas in cadmium acetate

solution. The rate of evolution of hydrogen sulphide was found to increase at higher temperatures.

A kinetic study of the rate of liberation of sulphur from reduced gypsum by steam was studied at 700, 800 and 900°C (Fig. 1).

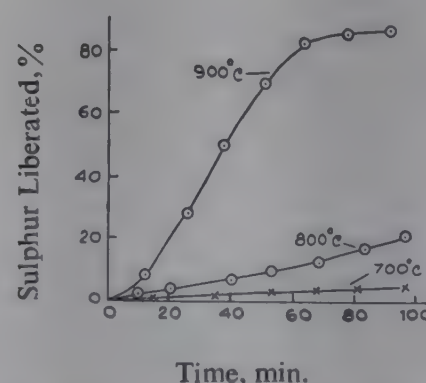


Fig. 1—Decomposition of Reduced Gypsum by Steam at Different Temperatures

In the second set of experiments instead of reduced gypsum, gypsum and coal in the ratio 2 : 1 was taken at 900°C and steam was introduced along with the carrier gas (nitrogen) at different time intervals, viz. (a) from the beginning (b) at 30 min. and (c) at 60 min. The results of liberation of sulphur are shown in Fig. 2.

It was observed that all the sulphur was not liberated as hydrogen sulphide but also as sulphur dioxide from reduced gypsum. A kinetic study of the liberation of these gases from calcium sulphide by the action

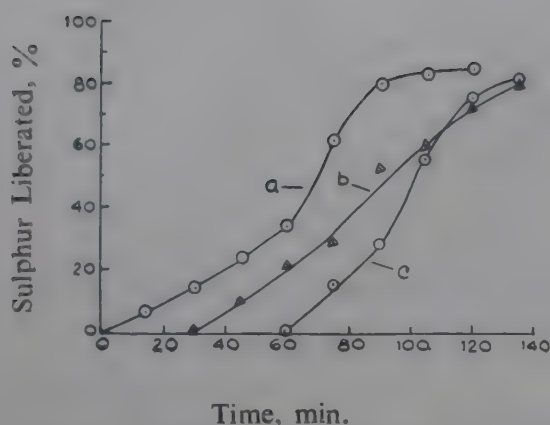


Fig. 2—Liberation of Sulphur from Gypsum-Coal Mixture by Steam at Intervals (900 °C)

of steam is shown in Figs. 3 (A and B). In this experiment, calcium sulphide was taken in a granular form of about 5 mm. size, and nitrogen was washed with alkaline pyrogallol solution to remove any oxygen present. Nitrogen was passed at a rate of 300 c.c./

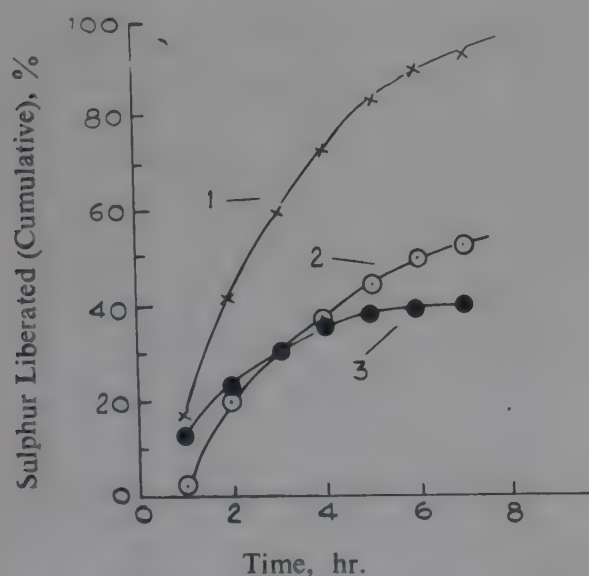


Fig. 3A—Liberation of Different Forms of Sulphur vs Time at 900 °C
1. Total Sulphur, 2. Sulphur as SO_2 , 3. Sulphur as H_2S

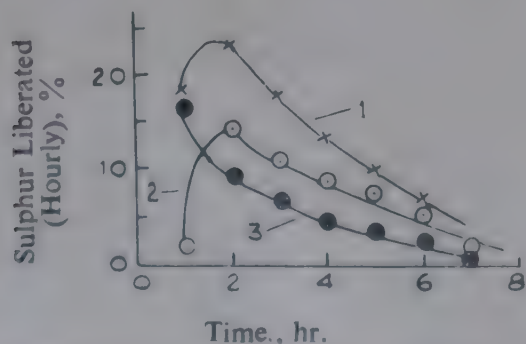


Fig. 3B—Liberation of Different Forms of Sulphur at 900°C
1. Total Sulphur, 2. Sulphur as SO_2 , 3. Sulphur as H_2S

min. which picked up steam from a steam vessel kept at 95°C. Fig. 3A shows the cumulative result of liberation of different forms of sulphur with time while Fig. 3B, a differential plot of the same experiment.

Results and Discussion

It was observed that liberation of sulphur from reduced gypsum by steam occurs at 900°C and above. The liberation is slow in comparison to that with carbon dioxide, as studied earlier². Instead of starting with calcium sulphide by reduction of gypsum, the process of reduction and subsequent steaming can be carried out in the same system, but this makes tar formation unavoidable.

Another drawback of the process was formation of hydrogen sulphide and sulphur dioxide gases though the reason of formation of the latter was not known. Fig. 3B shows that initially about 25 per cent of sulphur was liberated from calcium sulphide in a comparatively short time, but for the rest it was time-consuming. These results [Figs. 3 (A and B)] are much lower in comparison to that of Fig. 1, though both have been studied at the same temperature. This is apparently due to poor penetration of steam into the reduced gypsum granules.

Conclusion

The liberation of hydrogen sulphide from calcium sulphide by the reaction with steam takes place at about 900°C. This is a slow reaction. Both hydrogen sulphide and sulphur dioxide gases have been observed in the liberated gases.

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Copper-aluminium coprecipitated masses suitable for catalyst preparation have been studied by the conventional magnetic method. The specific susceptibility of copper in copper basic nitrate $3\text{Cu}(\text{OH})_2\text{Cu}(\text{NO}_3)_2$, was found to be 25.84×10^{-6} emu at 25°C . On magnetic dilution of the compound with aluminium hydroxide, the specific susceptibility of copper increased upto 44.81×10^{-6} emu. and the Weiss constants changed from zero to 75.

Effect of Aluminium Hydroxide on the Magnetic Properties of Copper Basic Nitrate

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Introduction

Copper-alumina catalyst is a well-known bifunctional system used in a variety of chemical reactions. It is used widely in the low temperature water gas shift reaction¹ and in the conversion of ethanol to ethyl acetate². Here, copper is the active ion and alumina acts as a dispersing agent or as a spacer between copper particles on the surface.

The spacers restrict the migration and the subsequent growth of the active crystallite particles, which also results in the modification of the crystal properties. Thus, the crystal parameters can be directly correlated with the polarizing strength (e/r) of the cations³ and hence with the catalytic activities. In the electronic sense a diamagnetic spacer, like alumina, raises the forbidden zone with the increase in the intercrystallite distances of the active ions on the surface of the support, facilitating the adsorption and catalytic processes. Such a role of the active particles and spacer substances is compatible with Balandin's geometrical relationship⁴ between interatomic distances in the reactant and the atomic spacing of the active species on the catalyst surface.

In the present study, an attempt has been made to correlate the spacer action of alumina and its magnetic dilution effects on the magnetic properties of copper ion in copper alumina system.

Experimental

Preparation of the samples: Electrolytic grade copper was dissolved in nitric acid (conc.), the concentration of this solution (A) being 14 per cent (w/v). In another vessel the required amount of aluminium nitrate (AR grade) was dissolved to prepare a 14 per cent (w/v) solution (B). Different proportions of the two solutions (A and B) were mixed and heated to 50°C , then precipitated with constant stirring by adding saturated solution of ammonium bicarbonate upto a pH of 6.5-7.0. The precipitate was washed and dried at 110°C for 5 hours in an air oven. Copper concentrations in the dried precipitates were estimated by the iodometric method. Alumina contents were estimated gravimetrically. The chemical analyses of the samples are presented in Table 1. Nitrogen content of sample A was determined by the Kjeldahl method.

Magnetic Measurements: A Faraday-type precision magnetic balance, constructed⁵ by the authors, was used for studying the thermomagnetic behaviour of the precipitates. The samples were heated to 120°C *in situ* to drive off the moisture prior to the magnetic susceptibility measurements. About 40 mg. sample was used and the instrument was calibrated each time with hydrated ferrous ammonium sulphate before measurements were taken on the samples.

TABLE 1—CHEMICAL COMPOSITIONS AND MAGNETIC PARAMETERS OF COPPER-ALUMINIUM CO-PRECIPITATED MASSES

Sample No.	Copper, %	Alumina, %	Specific Magnetic Susceptibility of Copper $\times 10^6$ at 25°C	Effective Magnetic Moment of Cu ²⁺ ion at 25°C	Weiss Constant	Colour
A	52.06	—	25.84	1.99	Zero	Green
B	46.60	7.55	30.02	2.10	+10	Bluish green
C	37.63	20.75	24.67	1.94	Zero	„
D	29.72	26.25	21.48	1.75	+20	„
E	17.32	37.25	22.45	1.73	+40	Blue
F	2.43	58.08	44.81	2.32	+75	Pale blue

Results and Discussion

The temperature dependence of magnetic susceptibility of paramagnetic materials is represented by the Curie-Weiss law,

$$X_M = \frac{C}{T + \Delta} \quad (1)$$

where X_M = Molar magnetic susceptibility of the magnetic ion,

C = Curie constant and is a function of the oxidation state of the magnetic ion,

T = Absolute temperature of susceptibility measurement, and

Δ = Weiss constant, which reflects the mode of electronic arrangement in the cationic neighbourhood of the magnetic ion.

Thus, according to equation (1) a plot of reciprocal specific susceptibility of the precipitate against temperature should be a straight line. Fig. 1 shows the Curie-Weiss law relationship of the precipitates between 25 and 120°C. Sample A on chemical analysis was found to contain about 25 per cent nitrogen and 52.06 per cent copper. Uchida et al⁶ prepared a basic copper nitrate and established the composition of the precipitate from X-R-D to be $3\text{Cu}(\text{OH})_2\text{Cu}(\text{NO}_3)_2$. On the other hand, while investigating the thermal and magnetic properties of the copper-chromium catalyst system, the present authors earlier reported⁷ a specific magnetic susceptibility of 11.48×10^{-6} emu with a zero Weiss constant

for the copper basic nitrate at 25°C. The calculated magnetic moment on the basis of the formula as well as the copper content was found to be 1.8 B.M. In the present case, chemical analysis of sample A also fits in the molecular formula of the copper basic nitrate. The specific magnetic susceptibility at 25°C was 13.45×10^{-6} emu with a zero Weiss constant. The calculated magnetic moment on the basis of copper content amounts to 1.99 B.M., which may be compared with 1.97 B.M. calculated on the basis of the molecular formula $3\text{Cu}(\text{OH})_2\text{Cu}(\text{NO}_3)_2$.

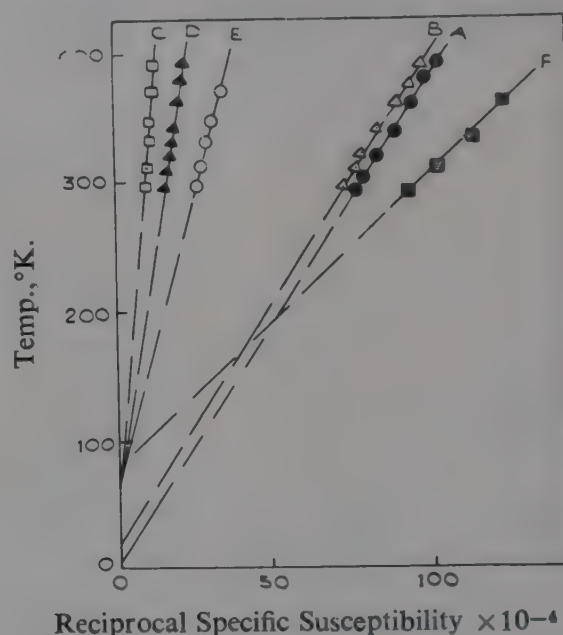


Fig. 1—Curie-Weiss Relationship of the Coprecipitated Copper-Aluminium.

The effective magnetic moments (Table 1) of Cu²⁺ ions in these samples at 25°C were found to lie between 1.73 and 2.32 B.M. Van Vleck⁸ reported experimental values of bivalent copper ions in the range 1.8-2.2 B.M.

It is well-known that on dilution by a diamagnetic material, the magnetic susceptibility values of a magnetic ion greatly increase due to the overcoming of the influence of the paramagnetic neighbourhood. This effect results in the change over of the Weiss constants from negative to positive values. The pure copper precipitate sample A does not show any inter cationic exchange interactions and is a purely paramagnetic material with a zero Weiss constant. In fact, this is the most magnetically concentrated sample of the series without any aluminium. Thus, considering all these factors it may be reckoned that the specific susceptibilities (Table 1) have been vitiated by the orbital angular moments only and not by the intercation exchange coupling. The positive Weiss constant values observed also confirm the absence of any intercationic exchange interaction. The orbital

angular moments are quenched to form the crystal lattice in a substance and hence become ineffective in contributing to the magnetic moment. Therefore, the effect observed here may be due to a variation in the lattice parameters of copper basic nitrate crystallites which has been caused by incorporating aluminium hydroxide as a 'spacer' material.

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An year round survey of the Godavari river water was made at Ramagundam in 1970 and 1971. The water was found moderately hard—magnesium exceeding calcium—and having a high pH and free from free carbon dioxide and non-carbonate hardness. It has an appreciable amount of sodium alkalinity and is free from any organic pollution. A primary treatment consisting of clarification-cum-partial softening in a clariflocculator has been suggested for making this water suitable for industrial process use.

Raw Water Characteristics of the River Godavari at Ramagundam

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The river Godavari, about 870 miles long, is the second largest river in Andhra Pradesh. It originates from the Western Ghats near Nasik (Maharashtra) and flows towards south-east mostly over the mineral rich black cotton soil of the peninsula and ultimately falls in the Bay of Bengal. It has four main tributaries, viz. Manjira, Pranrita, Indravati and Sabari. The river flows about 225 miles through Andhra Pradesh, which is the fifth largest State in India. In

Karimnagar district (Andhra Pradesh) Godavari passes by Ramagundam, where a coal-based fertilizer factory having a rated capacity of 1500 te/day urea is being set up by Fertilizer Corpn. of India. Its course is shown in Fig. 1.

As the proposed fertilizer factory at Ramagundam would draw its entire requirement of water (about 16.5 mgd) from Godavari, it was felt necessary to

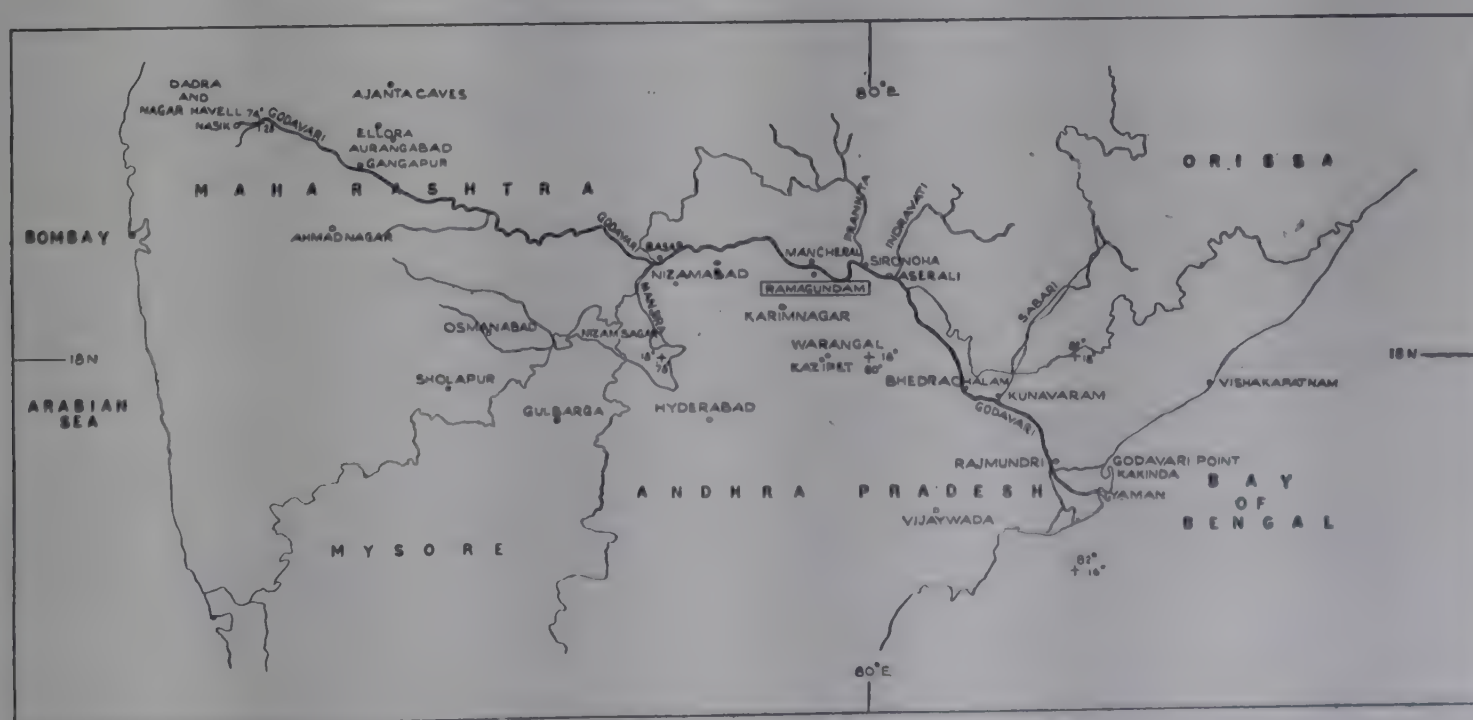


Fig. 1—Course of River Godavari

TABLE 1—ANALYSIS OF GODAVARI RIVER WATER
(Range of values in mg./l. unless otherwise stated)

Sl. No.	Month	Temp. °C	Turbidity	pH	Free CO ₂	Dis-solved O ₂	Alkalinity		Hardness		Dis-solved Fe	Chloride as Cl	Sulphate as SO ₄	SiO ₂	TDS.
							P	M	Ca ²⁺	Total					
1.	Sept. 1970	30 —33	1000 —4500	8.0 —8.2	4—6	7.2 —8.0	0.0	116 —136	60 —70	94 —112	0.10 —0.13	10 —13	9 —14	13 —16	165 —190
2.	Nov. 1970	35 —36	15 —20	8.4 —8.6	0—0	7.8 —8.0	4 6	170 —185	60 —62	130 —140	0.01 —0.02	16 —19	39 —42	20 —22	260 —280
3.	Feb. 1971	27 —29	15 —20	8.6 —8.7	0—0	8.1 —8.8	6 —8	210 —214	54 —60	159 —164	0.01 —0.08	33 —34	33 —42	16 —19	320 —340
4.	May 1971	31 —33	31 —33	8.5 —8.7	0—0	7.2 —8.2	5 —9	115 —187	50 —58	105 —130	0.06 —0.10	19 —22	60 —64	18 —21	256 —330
5.	June 1971	30 —32	80 —95	8.6 —8.8	0—0	7.8 —8.2	4 —6	160 —164	56 —60	128 —135	0.01 —0.02	23 —25	30 —48	20 —22	250 —290
6.	Sept. 1971	32 —33	120 —156	8.7 —8.8	0—0	8.0 —8.2	7 —12	124 —129	50 —60	98 —103	0.12 —0.15	12 —14	17 —20	17 —19	186 —200
7.	Dec. 1971	22 —23	20 —28	8.3 —8.5	0—0	8.2 —8.6	3 —6	184 —188	60 —63	135 —142	0.01 —0.04	24 —25	59 —71	12 —14	320 —340

N. B.—Alkalinity and Hardness are expressed as Calcium Carbonate.

evaluate the water characteristics of this river at Ramagundam. As no reliable data on raw water characteristics was available, an year round survey of the chemical characteristics of this river water was made in 1970 and 1971 covering all the important seasons.

Procedure

Samples of raw water were collected regularly from a fixed sampling point near the existing pump house of Singareni colliery's thermal power station. These were analysed in our field laboratory for pH, alkalinity (phenolphthalein and methyl orange), hardness (total and calcium), turbidity, dissolved carbon dioxide, dissolved oxygen, dissolved iron and temperature. The rest of the analyses were done in the main laboratory at Sindri. All the analyses were performed according to the standard method.¹

The results of the monthwise analysis (in range of values) are given in Table 1.

Discussion of Results

The data obtained in this survey indicate that the water of Godavari near Ramagundam is moderately hard, the magnesium component of hardness exceeding the calcium counterpart in most cases. Other

important features are higher pH and absence of free carbon dioxide and non-carbonate hardness. Alkalinity is significantly higher than hardness which indicates the presence of quite appreciable amount of sodium alkalinity. The chloride and sulphate contents are also somewhat higher than normally found in surface waters. Turbidity fluctuates widely only in the rainy season while in other seasons it is low showing insignificant fluctuation. A high dissolved oxygen content shows that the water is free from any significant organic pollution.

To make this water suitable for industrial process use the primary treatment should consist of clarification-cum-partial softening in a conventional clariflocculator with alum or other suitable coagulant and lime. The same clarified and partially softened water may be further filtered and chlorinated to make the same suitable for domestic use.

Acknowledgement

The authors gratefully acknowledge the guidance received from Sri G. S. Bhattacharyya, Asstt. Superintendent, while conducting this study.

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[Original mss. received on Dec. 4, 1974]

Redox potential and pH measurements were made in 2 soils (pH 5.60 and 6.70) at 5 and 15 cm. depth with and without paddy (IR-8) at different periods of submergence. Redox potential decreased, more sharply in the first 7 days and attained more or less a steady value in 30 days of submergence. Though the soil potentials were slightly higher at top 5 cm. than at 15 cm., no regular difference was noted between the different proximities of the root. Growing rice plant is found to have a depressing effect on reduction of soil in the immediate vicinity of the roots. Soil pH increased on flooding, more sharply in the first 7 days, followed by a gradual rise to a near-neutral value in 21 days of submergence.

Influence of Growing Rice Plant on Redox Potential and pH Changes in Flooded Soil

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Rice plant grows mostly under submerged condition that brings about a reducing environment in soil by restricting the entry of atmospheric oxygen¹. The oxygen necessary for respiration is transported by the aerial parts of the rice plant to roots². Many workers reported that the supply of oxygen from leaves to root may exceed the amount of oxygen consumed at the root³. The outward diffusing oxygen at the root surface partially oxidizes soil in the anaerobic root zone. The magnitude of oxygen passing to the root and out of it, and the extent to which the soil in the reduced root-zone is oxidized have not yet been established clearly, although unpublished observations of the authors indicate that they are confined to the soil in the immediate vicinity of root. Redox potential that measures the intensity of oxidation and reduction is an important parameter in the flooded soils and its measurements have been widely used to characterize the aeration in submerged paddy fields. The redox potential at the rice root-zone is likely to be influenced by the rate and amount of oxygen passing to the root and out of it. To get an idea of the effect of growing rice crop on the oxidation-reduction state in the immediately vicinity of roots, the present experiment was carried out to measure the redox potential and pH at different depths of submerged soil with and without crop.

Experimental

The two soil samples (0-15 cm.) used in this pot-culture experiment were collected from Ranchi and

Sindri. Some characteristics of the soils are given in Table 1.

TABLE 1—SOME CHARACTERISTICS OF THE SOILS

Locality	Texture	pH	E.C. mmhos/ cm.	Org. Matter, %	CEC, me/100 g.
Sindri	Sandy loam	6.70	0.70	0.62	12
Ranchi	-do-	5.60	0.25	1.17	15

5 kg. well sieved soil was taken in specially designed pots (30 cm. × 20 cm.) with holes (2 cm. diam.), large enough to insert sealed platinum electrode and combined glass electrode at 10 and 20 cm. from the top downward on the side of the pots. Altogether 12 holes were made, 6 at each depth, and rubber corks were used to close these holes tightly. The soil was submerged, puddled thoroughly, and nitrogen, phosphate (P_2O_5) and potash (K_2O) at the rate of 140-60-40 kg./ha were added in the form of urea, single superphosphate and muriate of potash. The following two sets (in triplicate) for each soil were prepared:

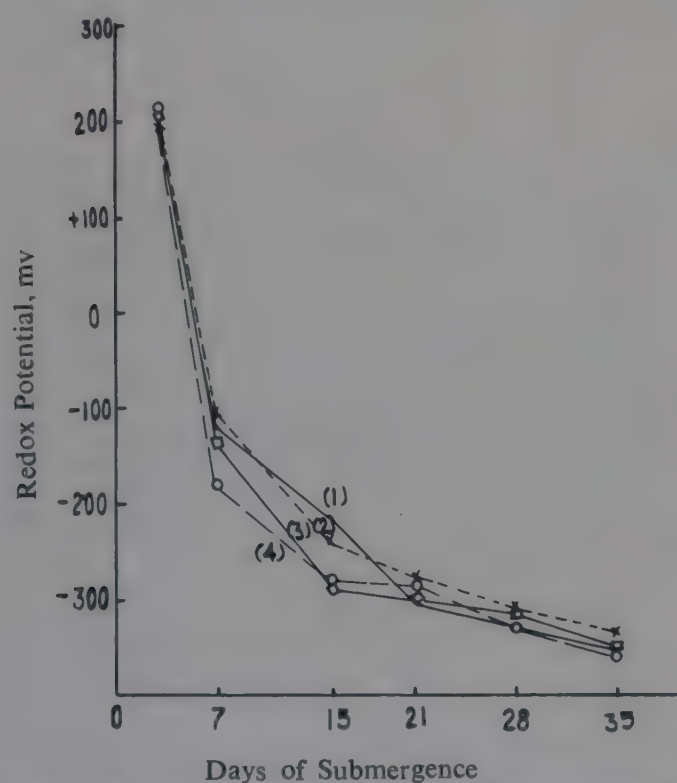
T_1 — Soil + 5 cm. standing water above the soil surface.

T_2 — Soil + rice seedlings + 5 cm. water layer. 21 days old IR-8 seedlings—2 in each pot were transplanted on the third day of submergence.

The measurements of redox potential (Eh) and pH were made at two horizontal distances (2.5 and 7.5 cm.) from the side of the pot towards the plant, i.e.

in the immediate vicinity of the root surface (7.5 cm.) and the other a bit away from it (2.5 cm.) at each depth on 3, 7, 15, 21, 28 and 35 days of submergence. Redox potential was measured by inserting sealed platinum electrode (Toshniwal make) through side holes and by dipping calomel electrode at the top and readings in millivolts were recorded 30 min. after setting of the electrodes. The platinum electrode was first inserted 2.5 cm. deep and after recording the Eh values, it was brought out, washed and inserted

Soil without Plant



again 7.5 cm. deep into the soil horizontally at the same depth. pH was measured by inserting the combined glass electrodes through the side holes after recording the Eh values. 6 similar holes at each depth were used for taking 6 observations.

Results and Discussion

The mean redox values (Eh) expressed in mv are represented graphically in Figs. 1 & 2. The results for pH are presented in Figs. 3 & 4.

Soil with Plant

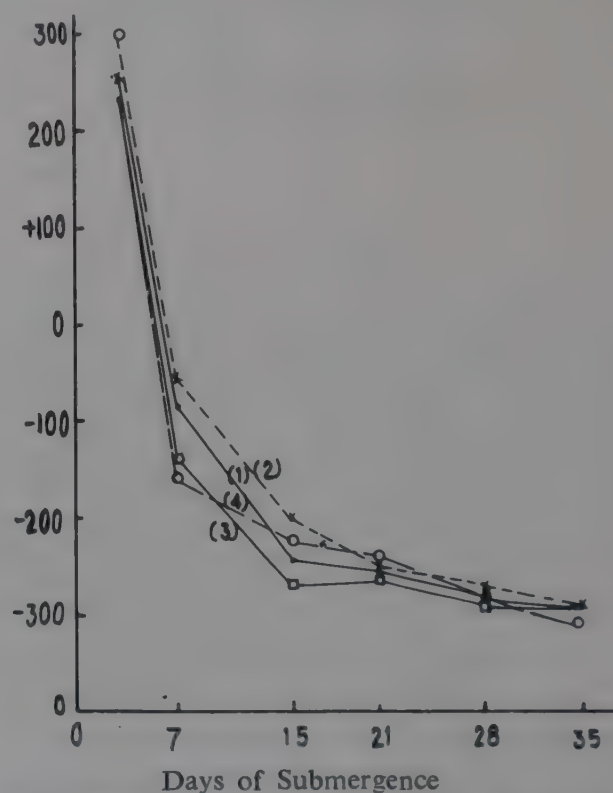
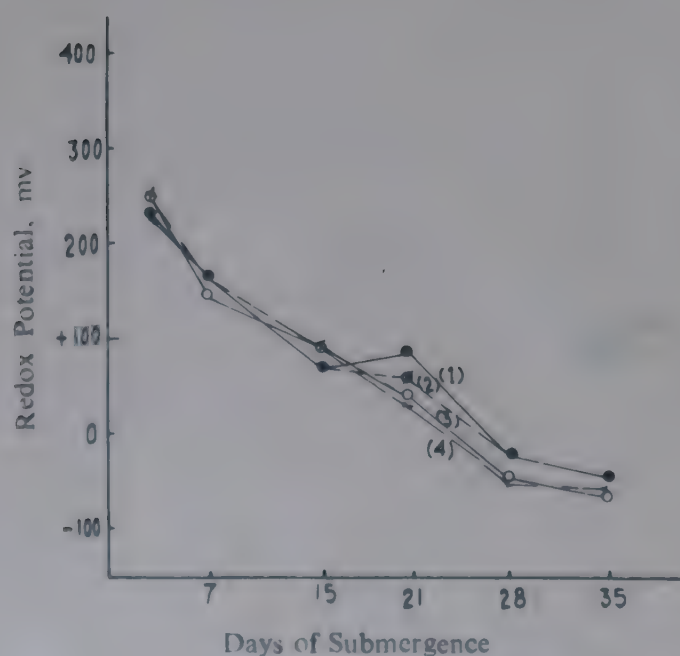


Fig. 1—Changes in Redox Potential with Days of Submergence (Sindri Soil) Legend (1) 5, 2.5; (2) 5, 7.5; (3) 15, 2.5; (4) 15, 7.5 (Soil Depth, cm.)

Soil without Plant



Soil with Plant.

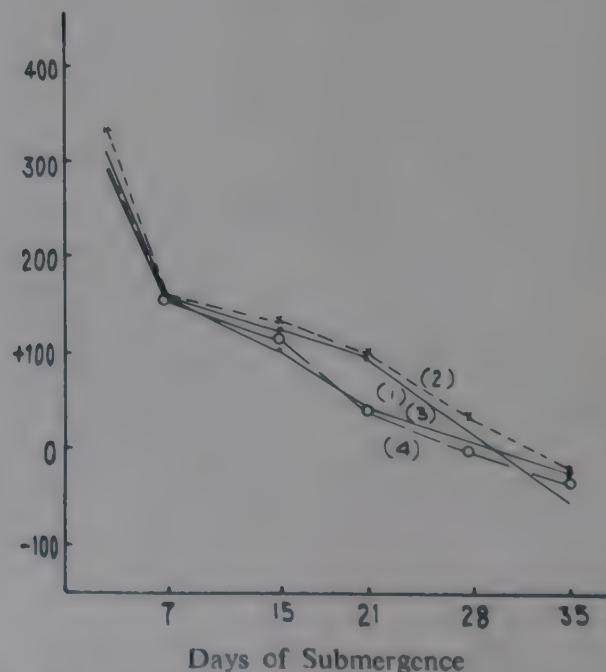


Fig. 2—Changes in Redox Potential with Days of Submergence (Ranchi Soil) Legend: (1) 5, 2.5; (2) 5, 7.5; (3) 15, 2.5; (4) 15, 7.5; (Soil depth, cm.)

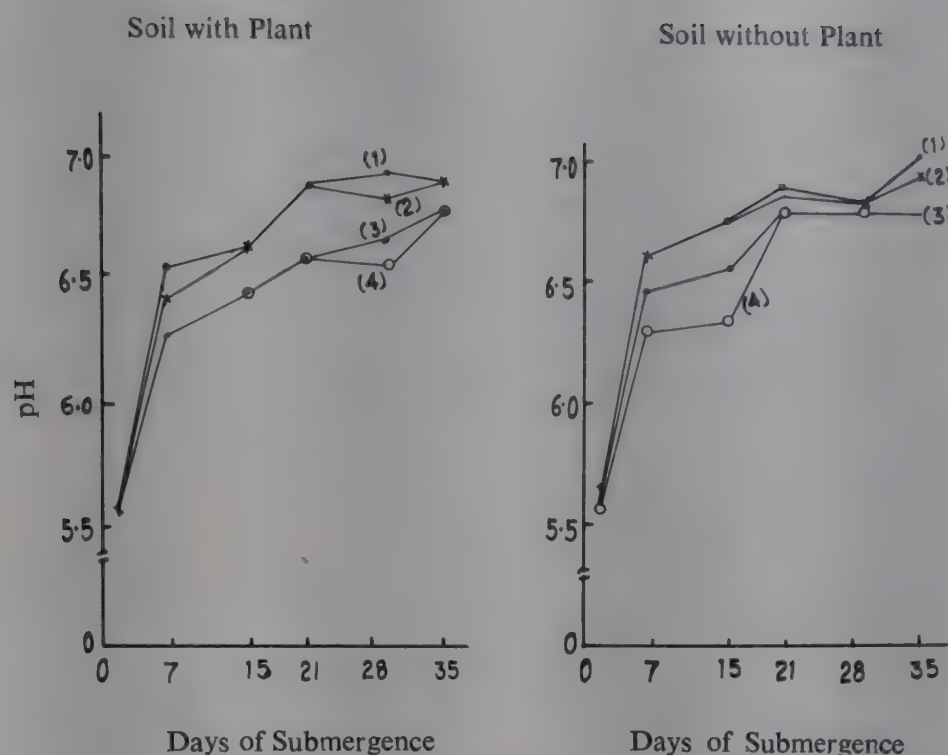


Fig. 3—Changes in pH with Days of Submergence (Ranchi Soil)
Legend
(1) 5, 2.5; (2) 5, 7.5; (3) 15, 2.5; (4) 15, 7.5 (Soil depth, cm.)

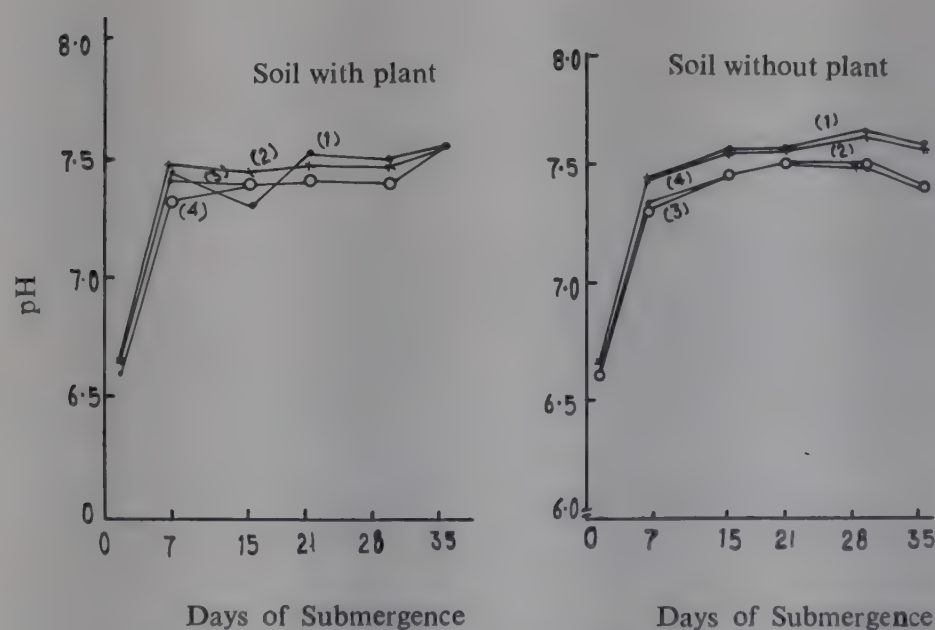


Fig. 4—Changes in pH with Days of Submergence (Sindri Soil)
(1) 5, 2.5; (2) 5, 7.5; (3) 15, 2.5; (4) 15, 7.5 (Soil depth, cm.)

Changes in Redox Potential: Redox potential decreased on submergence in all cases. The course of Eh was characterized by a sharp fall in the first few days, followed by a gradual decrease upto 21 days, after which it attained more or less a constant value. The magnitude of reduction, however, differed in two soils, reduction is greater in Sindri soil (+ 300 to — 400 mv) than in Ranchi soil (+ 330 to — 70 mv). The relatively lower magnitude of reduction in the lateritic soils of Ranchi was possibly due to its higher iron and manganese contents, which check the reduction rate.

The effect of soil depth on redox values was not very marked in either of the soils. During the first few days of submergence, Eh values did not differ much at 5 and 15 cm., but with increase in time soil potentials were noted to be higher in the upper 5 cm. than at the lower depth.

The growing of rice plant had a depressing effect on the reduction rate (Figs. 1 & 2). Redox potentials were found to be higher in the cropped soil than in the fallow soil. During the first few days, soil potentials were observed to be almost equal in the imme-

mediate vicinity of the root and a bit far from it. But with the development of root the potentials were noted to be higher in the immediate vicinity of the plant. The redox potential in the rice root zone was likely to be influenced by the oxygen involved in root respiration and photosynthesis. During the active vegetative growth phase, when photosynthesis was vigorous, the net result was likely to be the diffusion of oxygen out of the roots and consequently potentials are higher in cropped soil.

Changes in pH: Submergence led to marked increase in pH in both the soils under cropped and fallow conditions. An initial decrease of about 0.10 unit pH was noted in both the soils, possibly due to the generation of organic acids and carbon dioxide as the decomposition products of soil organic matter. In the Sindri soil, pH increased from 6.6 to about 7.5 in first 7 days and remained more or less constant for the rest of the period under study. In the Ranchi soil, pH increased sharply from 5.5 to 6.5 in first 7

days of submergence followed by a gradual rise to near neutral point in 21 days.

Depthwise pH was noted to be higher in the top 5 cm. of soil than at 15 cm. at any stage of flooding in both the soils. This might be due to the higher concentration of ammonium nitrogen generated from urea that is added to the top layer.

Growing plants do not have marked influence of soil pH under submerged condition and the pH values are found to be almost equal under cropped and fallow condition.

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The effect of soil application of three different doses of some NPK fertilizers (NPK 8:8:8=1.25, 2.50 and 5.00 per cent; Suphala 15:15:15=0.65, 1.30 and 2.60 per cent; Suphala 20:20:0=0.50, 1.00 and 2.00 per cent) on growth and flowering of soyabean was studied. The main-stem height increased significantly with 0.50 per cent of Suphala 20:20:0. There was an appreciable increase in the main stem node number with the application all the concentrations of NPK 8:8:8, 1.30 and 2.60 per cent of Suphala 15:15:15 and only 2.00 per cent of Suphala 20:20:0. The vegetative branches also increased significantly particularly with 5.00 per cent of NPK 8:8:8 and 2.60 per cent of Suphala 15:15:15. Leaf size and fresh weight of shoot, however, increased remarkably with all the treatments. No promoting effect was found on the flowering performances.

Studies on Soyabean [*Glycine Max* (Linn.) Merr.]

Part 1—Effect of Some NPK Fertilizers on Growth and Flowering

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Introduction

In India, soyabean cultivation has received limited attention,^{1, 2} due to the lack of adequate knowledge of its cultivation and fertilization. The yield response of soyabean to nitrogenous fertilizers has been studied by workers, like Norman³, Lathwell *et al*⁴, Wagner⁵ and Miyasaka *et al*⁶. Its response to phosphatic and potassic fertilizers has also been assayed by a few workers^{7, 9}. In this communication, the results of application of three different NPK fertilizers on the vegetative growth and flowering performances of this important crop have been presented.

Materials and Method

The seeds of soyabean, cv. Punjab type 1 obtained from U.P. Institute of Agricultural Sciences, Kanpur, were sown in unglazed earthenware pots containing three parts sandy loam soil and one part compost, thoroughly mixed. Almost all the seeds germinated within 7 days. The solutions of 1.25, 2.50 and 5.00 per cent of NPK fertilizer (8:8:8; ammonium sulphate, urea, phosphate and potash); 0.65, 1.30 and 2.60 per cent of Suphala (15:15:15; ammonium

nitrate, phosphate and potash) and 0.50 1.00 and 2.00 per cent of Suphala (20:20:0; ammonium nitrate and phosphate) were prepared by dissolving them in glass redistilled water. In the first treatment, 10 ml. of the solutions of all the fertilizers in question were applied on the surface of the pot-soil having 4-5 leaved, 19 days old single seedling per pot. Three successive applications of the same chemicals with the same concentrations but double in volume, i.e. 20 ml./plant/pot, were made to the same plant in the same manner at 10 days' interval. The control plants were treated with the same volume of glass-redistilled water. Ten plants of each treatment were randomly distributed and maintained under natural conditions in the college's botanical garden.

The vegetative growth was measured in terms of plant height, and the main stem node numbers at the following developmental stages were chosen arbitrarily, viz: (1) at 4-5 leaf stage when the first treatment was done; (2) at visible bud stage when the flower emergence took place. The height and node number

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of the different plants in the same treatment at stage 2 were measured on the day when the first flower bud was visible on the plant. At stage 3, i.e. at the complete blooming condition, the intact plants were uprooted and the branching (10 cm. and longer) as well as the average size of the nature leaf and fresh weight of shoot were recorded. Flowering (first flower) was measured by counting the number of days from the time of seed germination to flower emergence and the number of flowers formed when all the plants had reached the stage of complete bloom.

Results and Discussion

The results obtained are presented in Table 1.

Vegetative Growth: The plant height and node number at stage 1 were practically the same in all the plants, but with flower initiation a significant increase in the main stem height was obtained in all the treatments except the plants treated with 0.50 per cent solution of Suphala (20:20:0). Similarly, the plants treated with 1.25, 2.50 and 5.0 per cent solution of NPK fertilizer (8:8:8), 1.30 and 2.60 per cent solutions of Suphala (15:15:15) and 2.0 per cent solution of Suphala (20:20:0) showed a significant increase in the main stem node number

(Table 1). The vegetative branches (10 cm. and longer) also increased significantly in plants treated with 5.0 per cent of NPK fertilizer (8:8:8) and 2.60 per cent of Suphala (15:15:15). The remarkable increase in leaf size and fresh weight of shoot was obtained in all the treated plants, i.e. all the treatments increased the leaf size and fresh weight of the shoot significantly.

Flowering: The treatments had no significant promoting effect on flowering. The plants treated with 1.25, 2.50 and 5.0 per cent solution of NPK fertilizer (8:8:8), 1.30 and 2.60 per cent of Suphala (15:15:15) and 2.0 per cent of Suphala (20:20:0) significantly decreased the number of flower buds per plant (Table 1).

Thus, the above findings show that by the application of these different NPK fertilizers, the vegetative growth of the plants may be increased resulting in the production of more fodder. The higher doses of each NPK fertilizer appear to be more suitable for this purpose. It is also evident that the application of NPK fertilizers, particularly in higher doses, increase significantly the number and size of leaves resulting in an increase in the overall production of

TABLE 1—EFFECT OF THE APPLICATION OF DIFFERENT DOSES OF NPK FERTILIZERS ON GROWTH AND FLOWERING OF SOYABEAN (*Glycine max.* LINN.) MERR.

Fertilizer Treatments		Height at B Visible Bud Stage, cm.	Node Number at Visible Bud Stage	Average No. of Branches (10 cm. & longer) at Complete Bloom	Fresh wt. of Shoot at Visible Bud Stage, g.	Average Leaf Size (cm) at Complete Bloom, cm.	Days to Emergence of Flower Buds	No. of Flowers at Complete Bloom	Remarks
Control	0%	31.2	13.6	6.0	40.4	31.0	53.6	11.5	
NPK Fertilizer I (8:8:8)	1.25%	36.1*	15.7*	5.8	50.2*	41.0*	55.1	**6.7	
„ II	2.50%	39.2*	16.1*	6.4	72.6*	44.0*	55.9	**4.3	*Significant promotion
„ III	5.00%	42.1*	16.4*	7.6*	86.6*	58.0*	56.2	**2.2	
Suphala I (15:15:15)	0.65%	34.1*	14.1	6.6	55.8*	33.0*	55.4	11.0	**Significant inhibition
„ II	1.30%	35.5*	14.9*	6.6	61.4*	44.0*	55.2	** 8.7	
„ III	2.60%	39.5*	15.9*	6.8*	80.2*	51.0*	55.5	** 6.9	
Suphala I (20:20:0)	0.50%	33.0	14.0	6.4	46.4*	35.0*	53.1	11.6	
„ II	1.00%	34.9*	13.9	6.4	47.6*	40.0*	54.6	11.3	
„ III	2.00%	37.2*	15.7*	6.6	50.8*	41.0*	56.9	** 4.0	
F. Value	11.6	5.1	4.9	760.7	351.7	0.7	154.7		
C. D. at 5% level	2.5	1.2	0.7	1.6	1.2	Insignificant	0.8		
	+33.7 -28.7	+14.8 -12.4	+6.7 -5.3	+42.0 -38.8	+32.2 -29.8	— —	+12.3 -10.7		

leaves^{9, 10}. In this way, at least the green manuring quality of the plant can be enhanced.

Acknowledgements

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[Original mss. received on Dec. 8, 1973]

A method for the production of complex fertilizers from different Indian rock phosphates has been worked out. In this method the powders of rock phosphate and urea nitrate in the ratio of 1:2 were ground together for 2-3 hours. The resulting product gave more than 95 percent water-soluble P_2O_5 and can therefore be substituted for mixed fertilizer consisting of superphosphate and ammonium sulphate.

Production of Complex Fertilizers From Rock Phosphates

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Introduction

The conventional method of phosphatic fertilizer production requires the use of sulphuric acid in huge quantity. Many attempts have, therefore, been made to replace sulphuric acid by nitric acid in countries having no natural sources of sulphur. The investigations of Nydegger¹ for the production of water-soluble phosphatic fertilizer using rock phosphate are an important development in this direction. During recent years, Viswanathan² tried to develop a method to prepare nitrophosphate without the use of sulphuric acid at Neyveli. The recent discovery of huge deposits of rock phosphate in Rajasthan³ by the GSI prompted the present author to make a systematic study of nitrophosphate production from different Indian rock phosphates so as to assess the comparative fertilizer value of Rajasthan rock phosphate.

Experimental

Rock phosphates from Rajasthan, Uttar Pradesh and Bihar, obtained through Geological Survey of India, were powdered and sieved through a 100 mesh sieve (BSS). The powder passing through the sieve was analysed⁴ and used in the subsequent experiments.

Urea nitrate was prepared from urea (BDH) and nitric acid according to the procedure of Kutty and Murthy⁵. It was purified by recrystallization from water.

1 g. of rock phosphate was mixed with different amounts of urea nitrate and ground in an agate mor-

tar for 2 hours under dry conditions. The amount of P_2O_5 soluble when 1 g. of the mixture was leached with 250 ml. of water was taken as water-soluble phosphate. The amount of P_2O_5 soluble in 100 ml. of neutral ammonium citrate solution (sp. gr. 1.09 at 20°C) at 65°C in the residue after leaching with water was taken as the citrate-soluble P_2O_5 ⁶. P_2O_5 was estimated volumetrically after precipitating with ammonium molybdate solution⁷. The results are given in Tables 1 and 2.

Discussion

The analysis of different rock phosphates (Table 1) showed that the available P_2O_5 content with Rajasthan phosphate is maximum although Uttar Pradesh phosphate is richer in phosphatic content. It may be due to the fact that the former contained much more calcium phosphate than the latter which appeared to be richer in aluminium phosphate, and as the water-solubility of calcium phosphate is much more to that of aluminium phosphate⁸ more of P_2O_5 goes into solution.

The results (Table 2) indicated that with increasing urea nitrate content, the percentage of water-soluble phosphate increased and at the stage of 1:2 ratio nearly 98 per cent water-soluble P_2O_5 is obtained. On further increasing the amount of urea nitrate the percentage of water-soluble P_2O_5 first increases slightly and afterwards remains almost constant. Urea nitrate is an ionic salt while rock phosphates are basic and probably on grinding the mixture

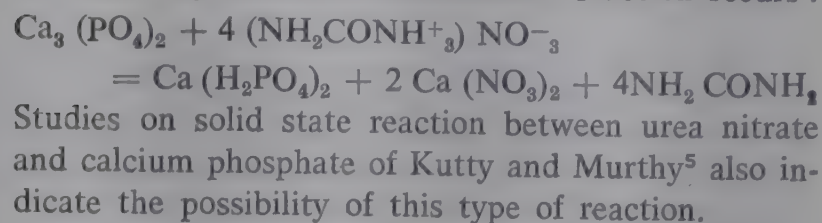
TABLE 1—ANALYSIS OF ROCK PHOSPHATES

Ingredients	Rajasthan Phosphates, %	Uttar Pradesh Phosphates, %	Bihar Phosphates, %
Insoluble Matter	5.60	3.24	24.14
Al ₂ O ₃	1.42	31.26	18.96
Fe ₂ O ₃	0.28	0.96	12.17
CaO	44.98	11.38	9.81
MgO	0.08	0.04	0.35
P ₂ O ₅	27.18	30.72	15.60
Available P ₂ O ₅	0.52	0.33	0.25

TABLE 2—WATER-AND CITRATE-SOLUBLE P₂O₅ IN ROCK PHOSPHATE UREA NITRATE MIXTURES

Rock Phosphate with Location	Rock Phos- phate to Urea Nitrate, wt ratio	Total P ₂ O ₅ , %	Water- Soluble P ₂ O ₅ , %	Citrate- Soluble P ₂ O ₅ , %	Frac- tion of Water- Soluble P ₂ O ₅ , %	Frac- tion of Citrate- Soluble P ₂ O ₅ , %
Rajasthan Phosphate (Jhamar- kotra)	1:0.50	18.12	1.4949	7.0613	8.25	38.97
	1:0.75	15.53	4.6434	7.1220	29.90	45.86
	1:1.00	13.59	6.2269	2.9789	45.82	21.92
	1:1.25	12.08	7.4823	2.1478	61.94	17.78
	1:1.50	10.87	7.6057	1.5109	69.97	13.90
	1:1.75	9.88	8.8850	0.2964	89.93	3.00
	1:2.00	9.06	8.8769	0.0815	97.98	0.90
	1:2.50	7.76	7.6482	0.0667	98.56	0.86
Uttar Pradesh Phosphate (Mussoorie)	1:3.00	6.79	6.7139	0.0570	98.88	0.84
	1:0.50	20.48	1.4499	7.9912	7.08	39.02
	1:0.75	17.84	5.2895	8.1885	29.65	45.90
	1:1.00	15.36	7.0041	3.3761	45.60	21.98
	1:1.25	13.65	8.4397	2.4392	61.83	17.87
	1:1.50	12.28	8.5665	1.7142	69.76	13.96
	1:1.75	11.17	10.0127	0.3406	89.64	3.05
	1:2.00	10.24	10.0229	0.0962	97.88	0.94
Bihar Phosphate (Itagarh)	1:2.50	8.77	8.6402	0.0771	98.52	0.88
	1:3.00	7.68	7.5816	0.0660	98.72	0.86
	1:0.50	10.40	0.7477	4.0560	7.19	39.00
	1:0.75	8.91	2.6507	4.0879	29.75	45.88
	1:1.00	7.80	3.5661	1.7113	45.72	21.94
	1:1.25	6.93	4.2882	1.2370	61.88	17.85
	1:1.50	6.24	4.3598	0.8698	69.87	13.94
	1:1.75	5.67	5.0859	0.1706	89.70	3.01
	1:2.00	5.20	5.0908	0.0478	97.90	0.92
	1:2.50	4.45	4.3850	0.0387	98.54	0.87
	1:3.00	3.90	3.8532	0.0331	98.80	0.85

the following acid-base neutralization reaction occurs :



Rock phosphates contain iron and aluminium phosphates, besides calcium phosphates and because of this reason cent per cent water-soluble phosphate is not obtained even with excess of urea nitrate.

According to the Indian agricultural experts, the water-soluble P₂O₅ has a definite superiority over the citrate-soluble in alkaline soils and for short season crops, whereas in acidic soils citrate-soluble P₂O₅ is as good as water-soluble phosphate². The production of mixed fertilizer with water-soluble phosphate will have this advantage. The complex fertilizer, being acidic in nature, is comparable with mixture of superphosphate and ammonium sulphate in matters of its effects due to pH. Moreover, as the process of production involves minimum number of steps, the cost of production will be reduced to a considerable extent.

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Fungi associated with the root regions of Arhar (*Cajanus cajan*) infected by pigeon pea sterility virus were assayed in contrast with their healthy counterparts. There was no difference in the total number of species associated with healthy and diseased rhizosphere. Certain fungi were confined to the rhizosphere either of the healthy or the diseased plants. Colony counts/g. of dry soil were more in the healthy plants than in the diseased ones. Association of certain potential pathogens with the root region of the diseased rhizosphere was noteworthy. Several *Penicillia* and *Aspergilli*, particularly the members of *Aspergillus ustus* group, were characteristic to the rhizosphere under both diseased and healthy conditions. The rhizosphere effect was more prominent in the case of healthy plants.

Microfungi at the Root-Soil Interface of Arhar [*Cajanus cajan* (Linn.) Mill sp.] Infected by Pigeon Pea Sterility Mosaic Virus

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Introduction

Morphological deformities caused by virus infection are well-known and are commonly associated with various physiological derangements in the plants¹. These disorders induce alterations in the micro-organic population of the root region of the plants²⁻⁵. The present communication incorporates authors observations on the rhizosphere fungal flora of a commercially important cultivar of Arhar (T-17) infected by pigeon pea sterility mosaic virus. Such an investigation is of great importance in understanding the nature of root disease pathogens in soil and in devising the control measures of the root-diseases.

Materials and Method

Plants of Arhar cultivar T-17 growing in the field (sandy loam soil) were chosen for the present study. Rhizosphere-free soil samples were collected at a distance of approximately 40 cm. from the diseased and healthy plants at post-flowering stage when nearly 3 per cent of the plants were showing sterility symptoms (profuse upright vegetative growth, absence

of flowering branches and small pale leaves) often marked with mosaic pattern^{6, 7}. The fungal populations were assayed by soil dilution plate technique⁸ using modified Warcup's medium⁹. The number of colonies appearing on the plates were noted and different species identified. Calculations were made for the percentage contribution of each species to the non-rhizosphere soils and for the colony counts/g. of dry soil as usual¹⁰. Healthy as well as diseased plants were uprooted and the superfluous soil along the roots removed. The rhizosphere fungal populations were studied by the procedure of Timonin¹¹. The observations were used for the calculation of percentage contribution of each species to the rhizosphere mycoflora and for colony counts/g. of rhizosphere soil.

The fungi associated with the rhizosphere region were studied by moist chamber method of Keyworth¹² by distributing the thoroughly washed root fragments in the moist chamber and incubating for a week at room temperature. The percentage composition and colony counts of rhizoplane fungi could not be determined due to obvious reasons. The number of

organisms in rhizosphere zone/number in root-free soil zone (R/S ratio) was determined in the usual way.

Results and Discussion

In all, 34 species were encountered from root regions of healthy and diseased plants. Some workers have reported considerably larger number of species in the rhizosphere of diseased plants than the healthy ones¹³ but in the present study, no such difference was found (Table 1). Of interest is the restricted association of a few forms either with the rhizosphere of healthy plant or with diseased ones. *Cladosporium herarum* and *Penicillium fumiculosum* appeared to have established themselves only with the rhizosphere of healthy plants, while *Fusarium moniliforme*, *Penicillium decumbens* and *Rhizoctonia solani* were confined to the rhizosphere of diseased plants

and were never isolated from the healthy rhizosphere. This may be connected with the nutritional factors. Probably a few limited species were specially favoured by the abundance of certain specific nutrients in the rhizosphere of the diseased plants, whereas some other species have a particular advantage in the root region of healthy plants. The nature of fungi at the root-soil interface is known to be chiefly governed by root secretion and redundant tissues of the root system¹⁴. Altered morphology and physiology of the plants should account for the difference in fungal composition in the root region of healthy and diseased plants.

The fungal population (colony count/g. of rhizosphere soil) was higher (Table 2) in the rhizosphere of healthy plants than in the diseased ones. This confirms the previous reports¹⁵ and may be ascribed to the inherent differences in the physiology of

TABLE 1—COMPOSITION OF FUNGI IN THE NON-RHIZOSPHERE, RHIZOSPHERE AND RHIZOPLANE REGIONS OF DISEASED AND HEALTHY PLANTS, %

Organisms	Healthy			Diseased		
	NR	R	RP	NR	R	RP
<i>Acremonium glaucum</i> Gams	3.4	—	—	3.8	—	—
<i>Acrophialophora fusispora</i> (Sak.) Sam.	5.3	—	—	6.0	—	—
<i>Alternaria alternata</i> (Fr.) Keis.	3.0	—	—	3.0	—	—
<i>Alternaria tenuis</i> Nees	3.2	3.0	—	1.3	0.2	—
<i>Aspergillus deflexus</i> Raper et Fenn.	1.8	2.2	—	3.3	4.0	—
<i>A. flavus</i> Link	6.7	5.0	—	3.5	4.6	—
<i>A. niger</i> Van Tiegh.	4.4	4.8	—	5.1	6.6	—
<i>A. ochraceus</i> Wilh.	2.1	3.2	+	—	0.8	+
<i>A. panamensis</i> Raper et Rhom	—	2.3	—	—	2.0	—
<i>A. puniceus</i> Kwon et Fenn.	—	2.5	—	—	4.1	—
<i>A. terreus</i> Thom	3.3	5.0	—	2.5	3.2	—
<i>A. ustus</i> Bain.	4.5	4.7	—	2.0	0.9	—
<i>Chaetomium apiculatum</i> Lodha	3.6	—	—	4.5	—	—
<i>Choanephora cucurbitarum</i> (Ber. et Rav.) Thaxt.	—	2.1	+	—	3.0	+
<i>Cladosporium herbarum</i> (Pers.) Link	5.4	4.3	—	—	—	—
<i>Curvularia genculata</i> (Wak.) Boed.	4.5	—	—	3.0	—	—
<i>Curvularia clavata</i> Jain	2.8	—	—	3.3	—	—
<i>Drachstera rostrata</i> (Dre.) Ric. et Fr.	3.8	5.6	—	5.9	2.7	—
<i>Drachstera spicifera</i> (Bain.) Arx.	—	1.4	—	3.1	5.0	—
<i>Fusarium moniliforme</i> Sheld.	—	—	—	1.2	1.7	+
<i>F. oxysporum</i> Schld.	—	3.0	+	—	3.2	+
<i>Humicola indica</i> Haw. et. Pav.	—	2.3	—	—	2.1	—
<i>Mucor hemalis</i> Wehm.	2.0	2.7	+	3.0	4.2	+
<i>Penicillium decumbens</i> Thom	—	—	—	—	3.2	—
<i>P. fumiculosum</i> Thom	1.7	2.7	—	3.7	—	—
<i>P. luteum</i> Zukal	1.8	3.6	+	—	4.0	+
<i>P. oxalicum</i> Curr et Thom	1.3	2.0	+	—	5.0	+
<i>P. variabile</i> Sopp.	1.8	4.0	+	3.8	6.5	+
<i>Phoma hybernica</i> Grim.	3.2	3.8	—	3.9	4.0	—
<i>Rhizoctonia solani</i> Kuhm	—	—	—	8.1	2.8	+
<i>Scopulariopsis brevicaulis</i> Bain.	2.8	3.5	—	1.0	1.2	—
<i>Thielavia sepedonium</i> Emm.	5.6	7.8	—	1.0	1.8	—
<i>Trichoderma viride</i> Pers. ex. Fr.	9.7	10.5	—	9.8	10.5	—
<i>Mycelia sterilia</i>	13.1	8.1	—	16.0	10.5	—

NR = Non-rhizosphere,
RP = rhizoplane,

R = rhizosphere
+ = presence,
— = absence.

TABLE 2—COLONY COUNTS G. OF NON-RHIZOSPHERE AND RHIZOSPHERE SOIL AND R/S RATIOS IN HEALTHY AND DISEASED PLANTS

Factors	Healthy Plant	Diseased Plant
Colony count/g. of soil (NR)	250100	260000
Colony count/g. of soil (R)	783000	395000
R/S ratios	3	1.5

diseased and healthy plants making the conditions more favourable for general fungal development in the volume of soil immediately around the roots of healthy plants. The moist chamber study revealed the association of a total of 9 species with the rhizoplane regions of the healthy and diseased plants. Of these, *Aspergillus ochraceus*, *Choanephora cucurbitarum*, *Fusarium oxysporum* and three species of *Penicillium* were of common occurrence both to healthy and diseased plants. There is evidence that many fungi, including species of *Aspergillus* and *Penicillium*, do not normally grow extensively through soil and find the organic remains more congenial for them^{16, 17}. It is also interesting that out of 7 *Aspergilli* isolated from the rhizosphere regions, 4 belonged to *Aspergillus ustus* group. Menon and Williams¹⁸ have already reported the abundance of the members of *A. ustus* and *A. ochraceus* groups when the soil was cropped to legumes. It will be worth while to determine the physical, chemical and biological determinants in congregation of these forms and the way these organisms interact with the microbial community in the rhizosphere of leguminous plants. Some species, like *Fusarium moniliforme* and *Rhizoctonia solani* were confined to the rhizoplane region of the diseased plants. Such a behaviour of potentially pathogenic species warrants further investigation.

The rhizosphere effect is more pronounced with the healthy rhizosphere than the diseased ones (Table 2). This can be attributed to the disordered physiology of diseased plants. Many workers have reported deviations in the carbohydrate content of the leaves and in the carbohydrate/nitrogen ratio as a result of virus infection^{19, 20}. This disorder affects the root system of the plant and as a consequence the rhizosphere mycoflora is greatly changed.

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Fungal flora from different flower parts, i.e. sepals, petals, stamens and carpels, and seeds of *Dahlia variabilis* Desf. have been investigated. Almost all the seed fungi isolated were obtained from the flower parts at different stages. A close correlation between the mycoflora of the flower and seed has been observed.

Mycoflora Associated with Flower and Seed of *Dahlia Variabilis* Desf.

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Mycoflora associated with the floral parts and seeds of soyabeans has been described by Kilpatrick¹. Some other reports available on the mycoflora associated with certain floral parts are of local interest (Welfswinkee², Plate and Schineider³ and Schenbeck⁴). Recently, Mishra and Srivastava⁵ found that fungi associated with floral parts of *Hibiscus rosasinensis* are nearly similar to those from the corresponding leaves. Local seeds of *Dahlia variabilis* are usually found to be associated with a number of fungi which affect the quality of the seed. The plant being an important ornamental one, an attempt has been made to trace the magnitude of seed infection by fungi associated with the different parts of the flower of *Dahlia*.

Materials and Method

Completely opened flowers of *Dahlia* were collected from the botanical garden of this University in sterilized glass containers and brought to the laboratory. All the floral parts (sepals, petals, stamens and carpels) were separated by sterilized forceps and collected in separate sterilized petri plates. Small pieces of equal dimension were cut with a sterilized razor. Equal number of pieces were introduced into 150 ml. conical flasks containing 50 ml. of sterilized distilled water. The flasks were shaken thoroughly for ½ hr. and water with spore suspension was inoculated on nutrient plates containing modified Martin's medium

for the study of loosely attached surface mycoflora. The flower pieces were then taken out and thoroughly washed with sterilized distilled water. The pieces after removing extra water by soaking them with sterilized filter paper were plated out on plates having PDA medium for the isolation of closely adhering mycoflora of the floral parts.

The seeds of the said plant were collected from a dried old flower in sterilized glass containers and mycoflora associated with the seeds were determined. The fungi from external surface of seed were isolated by the blotter method and also by plating on PDA. The seeds were presoaked for ½ hr in 0.01 per cent mercuric chloride solution and thoroughly washed with sterilized water before plating them in moist chamber and on PDA for the assessment of internal seed fungi.

Results

Quite a large number of fungi were cultured from the different parts of the flower. Amongst the 29 species isolated, only two, viz *Aspergillus niger* and *Alternaria tenuis* were of common occurrence. The number of species associated with sepals, petals, stamens and carpels was 19, 17, 11 and 21 respectively. Certain forms, viz. *Rhizopus nigricans*, *Mucor hiemalis*, *Chaetomium* sp., *Aspergillus niveus* and *A. fumigatus* (sepal), *Acremonium vitis* (petal), *Aspergillus tamarii*, *Humicola* sp. and *Epicoccum nigrum* (carpel), were of restricted occurrence and were isolated from the parts mentioned in the brackets. In all the sets, certain fungal species were specifically

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isolated either by washing method or directly from the flower pieces. Except for *Aspergillus niger* and *Alternaria tenuis* which were associated as common dominant or subdominant with the different parts of the flower, certain other fungal species of such category were of restricted occurrence (Table 1).

The distribution of the fungal species at different sampling dates was found irregular. A tendency, however, for increase in number of species at later stages was generally marked in all the sets except in the case of stamens and carpel by the washing method (Table 2).

Amongst the 13 fungal forms isolated from seed, *Aspergillus flavus*, *Curvularia pallescens*, *Alternaria tenuis* and *Fusarium oxysporum* were obtained both from external and internal portions. Ten species were cultured from external surface, whereas only 7 forms were obtained from internal region. Certain

forms were specially associated with external or internal regions only (Table 3).

Except *Fusarium nivale*, other 12 seed fungi were also obtained from flower parts at different sampling dates.

Discussion

Variation in the kind of fungi and their relative prevalence with different flower parts and the seed was observed. A large number of fungi, however, were associated both with the flower and seed. *Aspergillus niger* and *Alternaria tenuis*, which were dominantly or subdominantly associated with the flower parts, were also obtained as major fungi from external and internal parts of the seeds respectively. Similarly *Fusarium oxysporum* was also associated with both the substrates (Tables 1 and 3).

The above findings indicate clearly that the infection of the seed is caused mostly by the fungal spe-

TABLE 1—DISTRIBUTION OF FUNGAL SPECIES ASSOCIATED WITH THE FLOWER PARTS OF *Dahlia Variabilis*

Fungi Isolated	Sepal		Petal		Stamen		Carpel	
	W	D	W	D	W	D	W	D
<i>Rhizopus nigricans</i>		+						
<i>Mucor hiemalis</i>		+						
<i>Chaetomium</i> sp.		+						
<i>Aspergillus fumigatus</i>	+							
<i>A. flavus</i>		+	+++	+	+	+	+	+
<i>A. niger</i>	+++	+++	+++	+++	++	++	+++	++
<i>A. terreus</i>		++	+	++				+
<i>A. nidulans</i>	+	+	+	+			+	++
<i>A. aculeatus</i>			+			++	+	+
<i>A. niveus</i>		+						
<i>A. sydowi</i>	+	+	+			+		
<i>A. tamaraii</i>								+
<i>Penicillium</i> sp.		+	+	+++	++	+	+	++
<i>Acremonium vitis</i>			+					
<i>Verticillium terrestre</i>					+		+	+
<i>Trichothecium reseau</i>			+				+	
<i>Nigrospora sphaerica</i>							+	+
<i>Humicola</i> sp.							+	
<i>Cladosporium epiphyllum</i>	+	+		+	+	++	+	++
<i>C. herbarum</i>						++	+	+
<i>Curvularia lunata</i>	+	+	+				+	
<i>C. pallescens</i>	+	+	+	+				++
<i>Alternaria tenuis</i>	+++	+++	+++	+++	++	++	+++	+++
<i>A. humicola</i>	+++	+	++	+				
<i>Fusarium oxysporum</i>	+						++	
<i>Epicoccum nigrum</i>							+	
White sterile	++	+	+	+	+++	++	++	+
Black sterile	+		+			+	+	+
Yellow sterile				+				+
No. of species isolated by W and D methods	12	16	15	11	6	11	17	16
Total No. of species occurring on each floral parts.	19		17		11		21	

W=Washing method ; D=Direct inoculation ; +++=Dominant ; ++=Subdominant ; and +=rare.

TABLE 2—NUMBER OF FUNGAL SPECIES ISOLATED FROM DIFFERENT FLORAL PARTS ON DIFFERENT SAMPLING DATES

Sampling Dates	Sepal		Petal		Stamen		Carpel	
	W	D	W	D	W	D	W	D
March 10, 1973	7	5	7	5	2	6	9	8
March 30, 1973	5	5	5	5	4	2	11	8
April 20, 1973	8	10	12	5	0	5	7	9

W=Washing method ; D=Direct inoculation method.

TABLE 3—FUNGAL SPECIES ASSOCIATED WITH SEEDS OF *Dahlia Variabilis*

(Percentage occurrence)

Fungi Isolated	External		Internal	
	Blotter Method	PDA Method	Blotter Method	PDA Method
<i>Rhizopus nigricans</i>		29.72		
<i>Chaetomium</i> sp.	2.27			
<i>Aspergillus flavus</i>		2.70	25.0	
<i>A. niger</i>	15.90	48.64		
<i>A. tamarii</i>	2.27	2.70		
<i>A. niveus</i>			12.5	
<i>Acremonium vitis</i>	4.54			
<i>Curvularia pallescens</i>	4.54		50.0	
<i>Alternaria humicola</i>			54.54	
<i>A. tenuis</i>	20.45		18.18	
<i>Fusarium oxysporum</i>	50.0	13.51	18.18	12.5
<i>F. nivale</i>			9.09	
White sterile		2.70		
No. of species isolated from external and internal surface	10		7	

fungal species could, therefore, ultimately establish on the surface. Further, screening through seed coat gives access to the entry of a limited forms inside the seed tissue. Similar findings were also made by Kilpatrick¹ who studied the fungi associated with the flowers, pods and seeds of soyabeans. Mishra and Srivastava⁵ noted much commonness in the fungi of leaf surface and flower parts of *Hibiscus rosa-sinensis* for which they attributed to the similarity in the trapping habit and surface nutrients of the two habitats.

The chance of infection of the seeds is more in the later stages when the flower parts are in withering condition and are associated with more fungal species (Table 2). Plucking of the dead parts of the flower is recommended to avoid contamination of the seed to a higher degree.

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cies associated with the flower parts at its different stages. The different parts of the flower provide ample nutrients in the form of surface leachates to various microorganisms which happen to be trapped on their surface. As evident from the Table 1, carpel and sepal which are generally good seat for surface exudate encourage more fungal species (Table 1). The condition, however, is different in the case of the seed which is enclosed by the floral parts and only a few

Rhizosphere fungal populations of 10 weed plants (five each of Graminae and Cyperaceae) were studied by soil dilution and plate count technique. Most of the fungi were of common occurrence to the rhizosphere of both the plant groups. Certain forms showed their restricted occurrence to the root region of a particular group of plants, thus showing difference in the species composition. The plants of the same group also varied markedly in qualitative and quantitative nature of their rhizosphere fungi. Every plant itself appeared as a decisive factor in establishing the rhizosphere myco-population of its own.

Rhizosphere Micro-Fungi of Some Weeds

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Introduction

The generalization that soil micro-organisms are more abundant in the proximity of the root than at a distance¹, gave an impetus to the revival of interest in the investigations on the rhizosphere of various plants, and as a consequence a lot of information has accumulated²⁻⁴. It has also been well established that this enhanced activity in the root region is due to secretions of organic nutrients from the roots and sloughed away redundant tissues from the root surfaces which provide additional substrate for microbial decomposition⁵. Although this rhizosphere phenomenon is of great importance in understanding the behaviour of plant pathogens in soil and much is known about it, yet the knowledge regarding myco-organic components of the rhizosphere of weeds growing undesirably in the crop fields is still lacking.

In this paper, the authors have described their findings on the rhizosphere mycopopulation of 10 weed plants, 5 belonging to gramineae and 5 to cyperaceae growing in a low-lying paddy field in the vicinity of Gorakhpur University.

Materials and Method

Five graminaceous plants, viz *Eragrostis tenella*, *Setaria glauca*, *Dactyloctenium aegyptium*, *Cynodon dactylon* and *Digitaria bifasciculata*, and five cyperaceous plants, like *Cyperus rotundus*, *C. iria*, *C. tri-ceps*, *C. pumilus* and *C. compressus*, growing as dominant weed in a paddy field were chosen for the iso-

lation and study of the myco-organic population of their root region. The plants were uprooted, shaken gently so as to remove superfluous soil adhering to their roots. The root portions were separated and collected separately in clean glass containers. Equal amount of each root type was put in 500 ml. flasks containing 250 ml. sterile distilled water and shaken vigorously for 10 min. to make suspension of the soil clinging to the immediate root surfaces. After making suitable dilutions, 1 ml. of suspension of different root systems was transferred to *petri* plates (5 in each case) containing modified Martin's medium⁶. The plates were incubated at room temperature $22 \pm 5^\circ\text{C}$ for a week.

The fungi appearing on the nutrient plates were examined and identified. The data on the number of fungal colony per plate and the number of each species per plate were recorded and percentage composition of each fungus calculated. The colony count per g. of dry rhizosphere soil was computed by driving off the moisture in the original flask and weighing the contents, allowance being made for the amount of soil removed during preparation of dilutions. The percentages of fungi are presented in Tables 1 and 2. The colony counts/g. of dry rhizospheres of the plants are given in Table 3.

Results and Discussion

A total of 15 species were isolated from the rhizosphere of graminaceous plants while 21 species were

TABLE 1—PERCENTAGE COMPOSITION OF RHIZOSPHERE FUNGI OF GRAMINACEOUS PLANTS

Fungi	Rhizospheres, %				
	1	2	3	4	5
<i>Aspergillus aculeatus</i>	6.70	10.90	15.16	11.10	16.60
<i>A. flavus</i>	0.45	0.87	3.03	0.61	—
<i>A. flavipes</i>	—	0.28	—	—	0.50
<i>A. niger</i>	37.20	17.40	28.40	20.90	42.80
<i>A. niveus</i>	—	0.58	—	17.70	—
<i>A. terreus</i>	2.20	1.40	18.10	7.40	11.06
<i>Curvularia lunata</i>	9.01	3.18	3.03	20.30	5.00
<i>Fusarium</i> sp.	—	—	—	—	2.51
<i>Mucor hiemalis</i>	9.92	1.40	7.51	4.21	1.90
<i>Penicillium</i> sp. (white fluccose)	1.32	0.58	—	—	5.00
<i>Penicillium</i> sp. (white velvety)	—	0.58	—	—	—
<i>Penicillium</i> sp. (light green)	—	2.60	4.81	—	—
<i>Penicillium</i> sp. (dark green)	—	0.28	—	—	0.50
White sterile colony	21.60	—	—	—	—
<i>Trichoderma viride</i>	11.60	0.28	7.27	15.31	3.48

- 1 = *Eragrostis tenella*
 2 = *Setaria glauca*
 3 = *Dactyloctenium aegyptium*
 4 = *Cynodon dactylon*
 5 = *Digitaria bifasciculata*

TABLE 2—PERCENTAGE COMPOSITION OF RHIZOSPHERE FUNGI OF CYPERACEOUS PLANTS

Fungi	Rhizospheres, %				
	1	2	3	4	5
<i>Acrophialophora fusispora</i>	1.60	—	—	—	—
<i>Aspergillus aculeatus</i>	—	5.30	—	4.07	2.70
<i>A. carneus</i>	—	6.40	—	—	6.60
<i>A. flavipes</i>	2.20	4.90	0.50	0.50	5.75
<i>A. flavus</i>	1.90	2.10	—	2.53	6.07
<i>A. fumigatus</i> var. <i>ellipticus</i>	21.70	0.35	—	1.53	—
<i>A. niger</i>	12.29	7.80	1.17	10.23	10.31
<i>A. nidulans</i>	0.97	—	—	—	—
<i>A. niveus</i>	—	0.69	—	—	0.59
<i>A. tamarii</i>	0.32	—	—	—	0.30
<i>Chaetomium</i> sp.	—	6.40	—	—	—
<i>Chaetomium</i> sp. (white)	1.60	1.80	16.38	8.15	4.70
<i>Chaetomium</i> sp. (green)	0.63	—	25.73	14.30	—
<i>Curvularia lunata</i>	9.76	16.04	28.07	37.80	13.05
<i>Mucor hiemalis</i>	14.60	0.35	—	—	3.60
<i>Myrothecium</i> sp.	—	2.80	—	0.50	0.54
<i>Penicillium</i> sp. (light green)	7.60	24.10	10.52	10.23	22.05
<i>Penicillium</i> sp. (dark green)	2.58	7.40	10.52	—	0.30
<i>Trichoderma viride</i>	1.26	7.40	1.17	0.50	7.90
White sterile colony	4.50	3.50	4.68	6.61	—

- 1 = *Cyperus rotundus*
 2 = *Cyperus iria*
 3 = *Cyperus triceps*
 4 = *Cyperus pumilus*
 5 = *Cyperus compressus*

TABLE 3—TOTAL COLONY COUNT AND COLONY COUNT/G. OF RHIZOSPHERE SOIL OF DIFFERENT WEEDS PLANTS

Plant Rhizospheres	Colony Counts	
	Total Colony Count	Colony Count/g. Soil
<i>Eragrostis tenella</i>	261	4.6×10^4
<i>Setaria glauca</i>	408	5.8×10^4
<i>Dactyloctenium aegyptium</i>	205	7.4×10^3
<i>Cynodon dactylon</i>	185	3.2×10^4
<i>Digitaria bifasciculata</i>	232	4.2×10^4
<i>Cyperus rotundus</i>	308	9.1×10^4
<i>Cyperus iria</i>	285	1.2×10^6
<i>Cyperus triceps</i>	85	3.8×10^4
<i>Cyperus pumilus</i>	195	8.2×10^4
<i>Cyperus compressus</i>	419	2.1×10^6

isolated from the cyperaceous ones (Tables 1 and 2). Most of fungi isolated were common to the rhizospheres of both the plant groups. *Penicillium* sp. (white fluccose), *Penicillium* sp. (white velvety) and *Fusarium* sp. were restricted to the graminaceous rhizospheres. *Aspergillus carneus*, *A. fumigatus* var. *ellipticus*, *A. tamarii*, *A. nidulans*, *A. fumigatus* var. (white), *Chaetomium* sp. (green), *Penicillium* sp. *Myrothecium* sp. and *Acrophialophora fusispora* were confined to the rhizospheres of cyperaceous plants only. Thus, similarity as well as marked specificity in the species composition of the rhizospheres of the plants of two different families are evident. Plants of the same family favour the development of similar mycopopulation as reported by Kamal and Singh⁷. Similar exudation and moribund tissues from roots of the plants of the same family probably accounted for the commonness of the microfungi in the rhizospheres⁸. Kamal and Chaudhary⁹ reported similar amino acids from root extracts of two plants belonging to the same family and attributed the similarity in the rhizosphere mycopopulation to the presence of similar amino acids.

Plants of Graminae exhibited the common occurrence and high percentage contribution of *Aspergillus aculeatus*, *A. niger*, *A. terreus*, *Curvularia lunata*, *Mucor hiemalis* and *Trichoderma viride*. The rests of the forms showed their restricted occurrence to one or more rhizospheres. Likewise, *Aspergillus niger*, *A. terreus*, *Curvularia lunata*, *Penicillium* sp. (light green), *Chaetomium* sp. (white) and *Trichoderma viride* and white sterile colony appeared to be associated with all the plants of Cyperaceae. The

remaining fungal forms again showed their confinement to one or more rhizospheres. The common association of these species is further reinforced by their higher percentages. Thus, in the rhizospheres of the plant of both the families, there is further specificity.

It appears that a specific plant itself is a decisive factor in establishing its own specific mycoflora possibly because of chemical substances produced by the roots and the nature of sloughed off tissues of the root system¹⁰. The present findings also concur with those of Zukovsakaya¹¹, who claimed that each plant grown in the same soil enhanced the activity of a specific microflora of its own. It seems convincing that different species of the same genus or family stimulate the development of certain fungal types, the degree of preference being dependent upon the nature and amount of their root exudates and redundant tissues of the root system. The preferential development of certain fungal forms by different varieties of the same species has already been shown by Parkinson¹². The colony count/g. of rhizosphere soil and total colony count differed in different rhizospheres soil and total colony count differed in different rhizospheres (Table 2). Similar are the findings of Gangawane¹³, who noted considerable difference in the quality and quantity of fungal components of the rhizospheres of four different varieties of *Arachis hypogaea*. Similar reports have also been made by Rao¹⁴.

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Urea nitrate has been found to react with oxides of magnesium and calcium when ground together in the powdery form for 2-3 hr. The resultant product is completely water-soluble when the mole ratio of the oxide to urea nitrate is 1:2. This method can be utilized for manufacture of mixed fertilizer from urea nitrate and commercial calcium oxide obtained by burning dolomite.

Solid State Interaction Between Urea Nitrate and Oxides of Magnesium and Calcium

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Introduction

An increased productivity in agriculture can be achieved by application of improved cultivation practices. For this purpose, optimum balancing of the plant nutrients in successive application of fertilizers is essential. The production of mixed fertilizers containing available magnesium and calcium besides nitrogen and phosphorus has assumed great importance in this context. Whittaker *et al*^{1,2} have described a method of preparation of mixed fertilizers by reacting urea with calcium orthophosphate and gypsum. Schweiz³ claimed to have prepared a water-soluble phosphatic fertilizer by mixing intimately rock phosphate and urea nitrate. Recently, Pant and Pathak⁴ have developed a mixed fertilizer by interaction between urea nitrate and basic slag.

In the present investigation, an attempt has been made to prepare a mixed fertilizer containing water-soluble magnesium or calcium by grinding magnesium or calcium oxide with urea nitrate in the mole ratio of 1:2.

Experimental

1 g. mole of oxide of magnesium or calcium (BDH, A. R. quality) was mixed with different amounts of urea nitrate prepared from urea (BDH) and nitric acid⁵ and recrystallized, and ground in an agate mortar for 2-3 hr under dry condition (Table 1). In each case the resulting product was treated with pure

ethanol (99.8 per cent) and filtered. In the filtrate the amount of magnesium or calcium was estimated⁶.

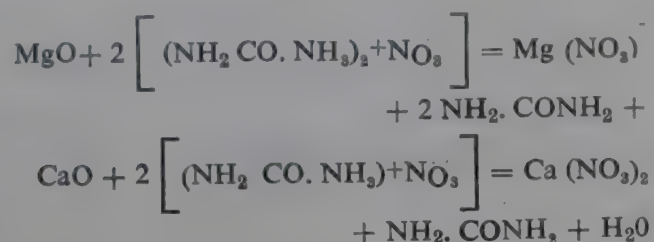
Table 1 —Soluble Magnesium/Calcium Content in the Product

Weight of Urea Nitrate, g.	MgO/CaO to Urea Nitrate, mole ratio	Mg (NO ₃) ₂		Ca(NO ₃) ₂	
		Calculated, g.	Found, g.	Calculated, g.	Found, g.
0.62	1 : 0.5	0.37	0.3256	0.41	0.3580
1.23	1 : 1.0	0.74	0.6956	0.82	0.7544
1.85	1 : 1.5	1.11	1.1048	1.23	1.2098
2.46	1 : 2.0	1.48	1.4704	1.64	1.6372
3.08	1 : 2.5	1.48	1.4782	1.64	1.6396
3.69	1 : 3.0	1.48	1.4800	1.64	1.6400

Discussion

The results (Table 1) show that with increasing urea nitrate content the percentage of water-soluble magnesium or calcium increases, and at the stage 1:2 ratio the solubility in both the cases reaches 99.8 per cent. On further increasing the amount of urea nitrate, the percentage of soluble magnesium or calcium increases only slightly and remains almost constant. This indicates that the oxides become almost completely water-soluble at the stage 1:2 mole ratio. In the initial stages, i.e. at 1:0.5 and 1:1, the percentage of soluble magnesium or

calcium is not much but at later stages it increases rapidly showing thereby that the excess of urea nitrate helps to increase the reaction. Urea nitrate is an ionic salt, while the metallic oxides are basic, and probably on grinding the mixture the following acid-base neutralization reactions occur :



In order to prove the above type of chemical reaction, the resultant product was treated with absolute alcohol in which the oxides are insoluble. The magnesium or calcium nitrate content in the ethanol extract increases with increasing amount of urea nitrate and reaches a limiting value when the mole ratio of the oxide to urea nitrate is 1 : 2. The limiting value of magnesium or calcium nitrate found corresponds to one mole for every mole of the oxide mixed with two (or more) moles of urea nitrate. This

clearly establishes the type of reaction, mentioned here.

For better crop yield soils require, besides nitrogen, potassium and phosphorus, magnesium and calcium. The commercial lime (obtained by burning dolomite) containing both calcium and magnesium may be used to prepare by the above method a mixed fertilizer suitable for nutrient deficient soils and for increasing fertilizer use efficiency.

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Cutting oil-water emulsions were found unsuitable as a fire-resistant hydraulic fluid in place of paraffin-based fluids, currently in use in hydraulic systems of gas generating plants, due to their poor lubricity, corrosivity, anomalous viscosity at higher concentration of oil and separation of scummy matter from them at high operational temperatures resulting in faulty pressure transmission in the system.

Substitution of Flammable Hydraulic Oils By Non-Inflammable Fluids

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Cases of hazardous fire in chemical plants using paraffin-based hydraulic fluids in hydraulic systems have been quite frequent. These are due to accidental leakage¹ or failures in pipes and joints with consequent spillage of oil on hot surfaces, where auto-ignition conditions exist.² As the modern trend is in favour of hydraulic power transmission owing to its efficiency and compact design, it is equally important to use a non-inflammable³⁻⁷ fluid in order to avoid costly damage to plants and machinery from accidental fires. Any fluid will burn under proper conditions but it is a question of determining the nature of the hazard prior to choosing a fluid. In addition to the flammability, it is also necessary to decide what service conditions it must satisfy.

Hydraulic systems used in warm conditions require a fluid with properties different from those under cold condition. Leaky, poorly maintained systems can function with less stable fluid, since replenishment is constantly required to replace leakage losses. Such being the conditions of the hydraulic system of the gas generating plant at the Sindri Unit of the FCI Ltd. it was considered worthwhile to investigate the use of a substitute which would be on one hand less expensive than the present fluid but on the other meet most requirements of a hydraulic fluid and be less hazardous. Some other conditions, which are usually most conducive for the outbreak of fire, viz.

the presence of carbon monoxide and coke breeze, both of which are likely to contribute adequately to flame-propagation and fire, are also present in a substantive amount in the gas generating plant. This initiated an investigation into the possibilities of replacing paraffin-based hydraulic oils by some other readily available materials, like cutting oil-emulsion in water, or glycerol-water mixtures having lower flammability.

The hydraulic system of the gas generating plant at Sindri has been basically designed to operate with a non-aqueous paraffin-based hydraulic fluid of specified viscosity rating of 145/155 S.U.S. at 100°F as met by DTE light oil, marketed by the Indian Oil Corporation. Other relevant characteristics,² which a hydraulic fluid is supposed to meet in addition to cost, are the following: (i) viscosity, (ii) viscosity index, (iii) stability towards oxidation, (iv) lubricity, (v) non-corrosive nature, (vi) compatibility to pumps, rubber seals, pipe-joints and paints, (vii) thermal stability at high operating temperature, (viii) non-foaming, (ix) low pour-point, (x) compressibility, (xi) non-clogging to filters, (xii) high flash-point, (xiii) low flame propagation properties, (xiv) non-toxic in case of skin contamination, and (xv) chemical stability.

ASTM, IP or equivalent ISI standards have not yet been drawn up on the characteristics⁸ of hydraulic fluids stated above or from the stand point of flam-

mability. As a result, fluid manufacturers have established their own tests and follow the guidelines indicated by the makers of hydraulic system. Water⁸ is not a suitable hydraulic fluid due to its poor lubricating value, low viscosity and consequent incompatibility with the efficiency of the pump of the hydraulic system besides corrosiveness to metal parts in master and slave cylinders.

Where fire-resistant fluids are to be used, their properties should be as near as possible to those of the mineral oil they are to replace. In a number of important properties, however, fire-resistant fluids differ significantly from mineral oil resulting, generally, in an unsatisfactory performance. The fire-resistant properties of the fluids were assessed by four tests, each of which gives information specific to a particular property, viz. (i) flash point, (ii) fire point, (iii) auto-ignition temperature, and (iv) flame propagation. Substitution was, therefore, considered necessary.

Experimental

Accordingly, the problem was taken up in conjunction with the Sindri Unit of FCI Ltd. to investigate the usage of emulsion type (cutting oil in water) fluids as hydraulic fluids. Most of the experimental tests were carried out on a bench unit of the hydraulic testing laboratory attached to the gas plant, while the laboratory tests were conducted in the P & D Division. Operational tests were carried out with and without load on the No. 7 generator of the plant. Emulsions of SOLVAC and DROMUS⁹ with water were prepared with varying proportions of oil and water tested for the requisite properties as enumerated earlier. Viscosities of different emulsions as determined are given in Table 2.

Foaming tendencies were observed during preparation of the emulsions with SOLVAC with water (noted particularly while pouring the emulsion into the reservoir or during mixing with water), which required to be counteracted before using it for the operational tests in the plant.

Stability² of the different emulsions was studied in the laboratory and it was observed that there was a tendency for all the emulsions to deposit small quantities of brownish oily matter, as also floating coagulated mass above an emulsion temperature of 70°C (scummy matter also appeared due to aerial oxidation on the surface of emulsion as the fluid-reservoir in the bench unit was exposed to the atmosphere). In this connection, it may be worth while to indicate that viscosity, which is also a lubricating property, is a function of the stability of the emulsion at the operating temperature. Chemical stability of a hydraulic fluid is thus a determining factor of its useful life.

Corrosivity, as envisaged in such emulsions, was investigated by the accelerated test methods which showed apparently no sign of corrosion upto 1 hr. but beyond that, slight corrosive tendencies were observed in case of mild steel at 160°F.

The fire point of SOLVAC (without emulsification with water) was observed at about 500°F. Due to the presence of water in an emulsion form, the flash point of SOLVAC could not be determined. Similarly, water-emulsions of SOLVAC gave no flash point. It may be mentioned here that the flash-point of Mobil DTE (Light) was 395°F.

For obtaining actual performance data for the use of cutting oil emulsions in hydraulic systems, closely resembling plant conditions, a trial was carried out

TABLE 1—CHARACTERISTICS OF DIFFERENT OILS

Sl. No.	Oil	Sp. Gr. at 60°F	Viscosity		Flash Point, °F	Max. Pour Point, °F	Remarks
			100°F SUS	SUS			
1.	D.T.E. Oil Light M/s. I.O.C.	0.871	145/155	43.4 at 210°F	395	20	
2.	Cutting Oil (SOLVAC) 1535 M/s. I.O.C.	0.9303	359	100/120	*—	—	Specified by the manufacturers as suitable for use in water/hydraulic systems.
3.	Cutting Oil (Dromus Oil B) M/s. B.O.C.	0.941	311	—	—	—	

* Flash point of cutting oils could not be obtained as the product contained water (Report was sent by the Lubrication Section, F.C.I., Sindri Unit).

TABLE 2—VISCOSITIES OF DIFFERENT EMULSIONS

Sl. No.	Emulsions			Viscosity at 100°F		Minimum Quantity of Defoamer Required for Appreciable Effect on Controlling the Foam, % by vol.
	Solvac % by Vol.	Dromus % by Vol.	Water % by Vol.	Red Wood-1	SUS	
1.	30	—	70	53.2	37.5	
2.	40	—	60	39.5	44.0	0.2
3.	45	—	55	48.0	55.0	0.3
4.	50	—	50	73.5	83.0	0.5
5.	55	—	45	97.0	111.0	0.8
6.	57	—	43	112.5	128.0	1.0
7.	58	—	42	161.0	183.0	—
8.	60	—	40	240.0	270.0	—
9.	—	40	60	38.1	43.0	0.2

on the test bench of the gas generating plant workshop. An emulsion of 45+55 (SOLVAC: water) was used in the trial run and the system was kept running for several days. The basis for choosing the particular ratio of SOLVAC: water for preparing the emulsion was that the viscosity of a higher concentration of oil-in-water emulsion is anomalous,¹⁰ which was established from laboratory trials with various proportions of the components. The performance seemed to be satisfactory during the first part of the trials for a week-long run but foaming with consequent vapour-locking and loss of pressure was observed. The loss of pressure in the system was due to (i) foaming and consequent vapour-locking and (ii) low viscosity of the emulsion (55 SUS at 100°F) as compared to Mobil DTE (Light) hydraulic oil (145-155 SUS at 100°F).

Since the bench test unit did not have any in-line filters, the separated scummy semi-solid mass could not be removed on formation and it worked its way into the pilot valves of the slave cylinders which were being used for the trial runs. It was therefore conjectured that plant trials, where in-line filters were incorporated, would possibly obviate the difficulties encountered due to scum formation. Trials, with similar emulsions, were embarked upon in the No. 7 unit of the gas generating plant without load in the first phase in order to observe pressure build-up and valve operation. On-load trials were decided to be carried out at a later stage after attaining stability of operation without load. The performance was all along watched closely.

After 12 hours' trial run without load and on reaching a certain degree of stability, on-load conditions were introduced. On the same day, after 18 hours' running of the system on load it was observed that there was an appreciable loss of power transmission due to quick fall in pressure accumulated. Subsequent make-up of pressure was tardy.

Excessive foaming was also observed and there were leakages from many joints and fitting apparently contributing to the pressure loss. The bleeding of the lines was carried out regularly to counteract vapour-locking due to foam formation. Scummy matter, which did appear in the reservoir, ultimately choked the filter located in the return line of the pump. Subsequent installation of two sets of filters did not help to obviate the difficulties. All these gave a clear indication that the prepared emulsion was chemically unstable^{11, 12} and possessed low-viscosity apart from the excessive foam forming tendencies.

The control of foaming was subjected to further investigation, and a silicone-based defoamer¹³ was found to be partially effective in its defoaming action. The quantitative effect of the defoamer on various ratios of SOLVAC: water emulsions is indicated in Table 2. The additives were not used, as the primary requirements of hydraulic fluid used in generators were not fulfilled by the emulsion.

Discussion and Conclusion

From the observations in the plant as also in the laboratory trials, it appears that such emulsions are unsuitable for use as hydraulic fluids in hydraulic systems where lubricating values, corrosion to metal parts, foaming, clogging of filters, frequent bleeding of lines and deposition of scummy matter in the fine orifices of the slave and master cylinder valves are too frequent and need constant attention and rectification for a smooth operation.

Current literature¹⁶ reveals that a hydraulic power transmission unit is not devoid of lubrication requirements and the modern trend is for using water-in-oil emulsions, rather than oil-in-water, as the hydraulic fluid. With water-in-oil^{10, 11, 14} emulsions, the propensity of lubrication is much more due to the oil being the dispersion medium. Inasmuch as emulsions entail the usage of soaps, foaming and frothing should be almost negligible as vapour-locking is caused by foams resulting in a faulty pressure build-up and consequent transmission of power. Since

emulsions are subject to the relative instability of such liquids, care must be taken to see that they are made and used under conditions ensuring optimum stability. Lower lubricity in hydraulic pump applications may also be observed while using such emulsions.

The use of phosphate esters and chlorinated biphenyls^{1, 5, 15} blended with mineral oil has been used as hydraulic fluid in places where chances of accidental fire due to spray from leakages are prevalent. Such synthetic fluids have been reported to be extremely costly on the one hand and toxic, on the other, in case of prolonged skin contact. Such synthetic hydraulic fluids have also been reported to have poor hydrolytic stability and even traces of moisture may cause hydrolysis of fluids. Since, ambient conditions in our country are usually hot and humid, the use of such hydraulic fluids remains out of question as it would be extremely difficult, if not impossible, to have a completely sealed, locked-in system precluding moisture.

Water-glycol mixtures have been reported as excellent fire-resistant hydraulic fluids and no combustion or flame-propagation has been said to have occurred when subject to the spray flammability tests on a hot plate kept at 1200°F. Such glycols and or polyalkylene glycols^{3-7, 15} and water plus specific amounts of inhibitors oilness agents, and film-strength additives form stable solutions and meet most requirements of hydraulic fluids discussed earlier, except being incompatible with zinc and cadmium. Aluminium should be anodised, if used. Such mixtures have the requisite oxidative, thermal and hydrolytic stability normally needed of hydraulic fluids and the advantages weigh out heavily in favour of using such solutions as a fire-resistant fluid in the hydraulic system of the gas generating plant at Sindri. The use of ethyleneglycol as an anti-freeze in heat exchangers and radiators of internal combustion engines is well-known and it would be an effective replacement for mineral oil-based flammable hydraulic fluid as is being used currently.

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Some run-of-mine samples from Surakachhar and Banki collieries of Ghordewa sector, Korba, have been analysed. These analytical data are essential for the design and operation of the gasification plant of the Korba fertilizer project. The overall coal is expected to have a consistent ash content in the range 18-23 per cent on dry basis. The ash content has been compared with that of the available borehole samples of coal in the adjacent area. The screen analysis given may indicate possible size distribution and ash content. The ash is refractory in nature.

Studies on Ghordewa Sector Coal for the Korba Fertilizer Project

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The Korba fertilizer project dates back to the recommendation of the Kane Committee in 1960. In 1962, FCI Ltd. selected Korba as the most suitable place for a coal-based fertilizer plant from the point of view of proximity to raw materials and utilities, like water and electricity. Based on the analysis of a large number of r.o.m. and borehole coal samples from Rajgammar coalfield¹ several feasibility reports were prepared by the FCI Ltd. But in July 1965 the Government of India decided not to proceed with the project in view of a relatively higher investment cost of a coal-based project as compared to one based on naphtha. However, the project was again reviewed and final approval to it was given by the Government in 1969. Simultaneously the two coal-based fertilizer projects at Talcher and Ramagundam were also approved.

It has been estimated that by 1978-79 the northern zone will be deficient by one million tonne of nitrogen.² The coal-based fertilizer factory being set up at Korba in Madhya Pradesh will considerably reduce the gap between demand and supply.

A coal-based fertilizer plant has to be located almost on the minehead, thus reducing transport and handling costs. The National Coal Development Corporation (now C.M.A. Ltd.) has already built up

in Surakachhar colliery a large production capacity, viz. a million tonne of coal per annum at an investment of Rs. 9 crores. The adjoining Banki colliery of CMA has a production target of 0.6 million tonnes, which would serve as a captive mine for the fertilizer project. The finished product, urea, would be carried about 40 km. to Champa and distribution of the finished product from such a central inland location will cover almost 360° degrees.

Process

Like the Talcher and Ramagundam projects, Korba will have a capacity of 900 te/day ammonia. Adopting Koppers-Totzek process of total gasification of pulverized fuel (80 per cent through 200 mesh) at a slightly above atmospheric pressure using 90 per cent purity oxygen and steam, the reaction would be carried out in three gasifiers in suspension in a co-current flow of oxygen and steam admitted through nozzles at about 1600°C. To aid the slagging of ash, the addition of flux may be done at the grinding stage. Each gasifier will have a raw gas output of 27800 NM³/hr, of CO+H₂ (equivalent to 12.5 te ammonia). The mixture of raw gas and unreacted steam will flow upward and agglomeration of ash particles that are too heavy to remain in suspension will fall

into the dust leg in a molten condition. The gases would pass through a waste heat boiler at 300°C and will be further cooled down to 40°C before their dust content is reduced to 6-14 g./NK³ in a scrubber. These will be followed by Thyssen washers and two sets of electrostatic precipitators to get a clean cool gas with dust content reduced to less than 0.2 g./Nm³. The raw gas will then be compressed to 31 atm. for desulphurization, which would be followed by CO-conversion, removal of carbon dioxide by Rectisol process and final purification by washing with liquid nitrogen. The gas will then be compressed and sent to the ammonia synthesis loop.

The smoothness of operation and the consumption of oxygen and coal will depend on the characteristics of coal, like ash content, ash fusion character, grindability, etc. The availability of coal of known characteristics from the various coal seams located near the site as well as prediction of future coal supplies from the same area require a thorough study of the geology and borehole study of the coalfield.



Fig. 1—Map of M. P. Showing Korba & Other Important Coalfields.

Geology

Ghordewa sector, situated on the western side of the Hasdeo river, is a narrow strip, 3 km. × 14.5 km. Of this sector, an area of about 28 sq. km. (22°-20'-30"—22°-24'-10" N and 82°-35'-10"—182°-41' E) is the potential coal bearing area, which falls mainly under Blocks I and II.³⁻⁶

Seven coal horizons have been met in this area and the two seams, viz. G-I and G-III, are most important having a suitable thickness and fair quality coal. The entire strata of the area consists of lower Barakars generally dipping towards south and south-west, the dip being of the order of 7° towards south and 3-4° in the central and western area. The sequences of the seams from top to bottom are G-IV, G-III, R-I, G-IIA, G-II, G-I and G-IA. In the western side of the sector, G-II has developed very poorly so that seam G-I is directly met under G-III. Here the parting between G-III and G-I is 62-73 m. in the outcrop to 82-84 m. in the extreme dip area. In the eastern side, the parting between G-III and G-II is about 43-48 m. in the outcrop to about 50-58 m. on the extreme dip. In the middle of the sector the parting between G-III and G-II is 45-50 m. The parting between G-I and G-II seems, is of the order of 17-25 m.

The entire coalfield is covered by a number of faults, which strike either oblique or dip. They are more or less straight and are of normal types. Some of the important faults are shown in the map (Fig. 2), in which a number of boreholes investigated in the past are also marked.

The entire Ghordewa sector is covered by two collieries, viz. Surakachhar and Banki, both operated by CMA. So far, only the G-III seam has been developed for production at both the collieries. The development of the G-I seam is proposed to be taken up in the near future. The total coal reserves are estimated at 38 and 35 million tonnes for G-I and G-III seams respectively. The phased working plan of this sector by the CMA are shown in Fig. 3.

Experimental

The present study has been concentrated mostly on the coals of Surakachhar colliery, which is expected to supply 90 per cent of the requirement of this project. Any shortfall will be met from the Banki colliery. R.o.m. coal samples were collected from the working areas of the two collieries periodically round the year. Three seam samples were also collected. In the preparation of the samples, shales below 4" were not separated. Each sample was tested for proximate and ultimate analyses, calorific value and ash fusion temperature. Table 1 gives proximate analysis of the samples on air-dry, dry and dry ash free basis. Table 2 gives the ultimate analysis and calorific value. The various characteristics,

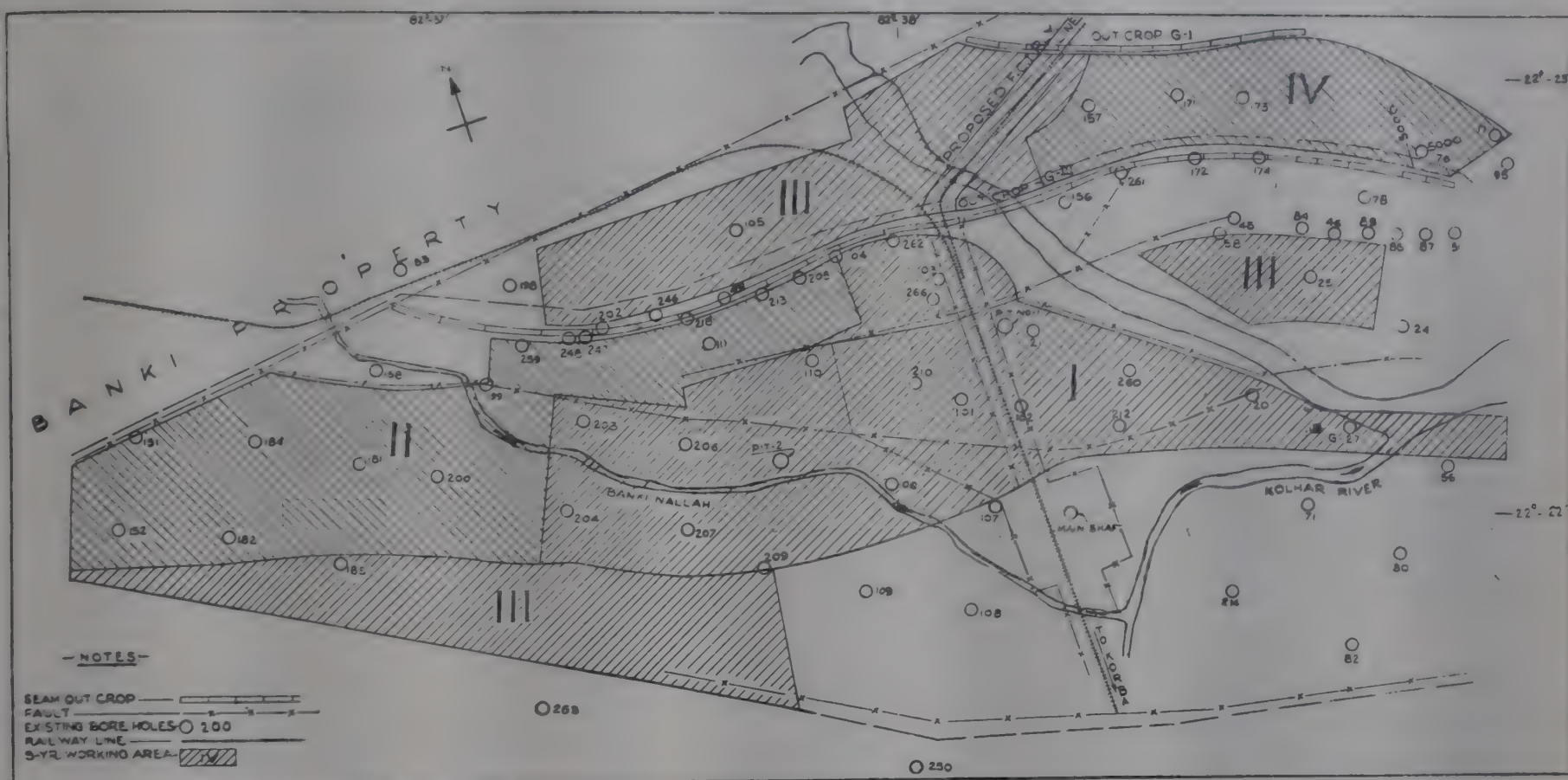


Fig. 2—Working Plan of Coal Mining Authority for Surakachhar Colliery.

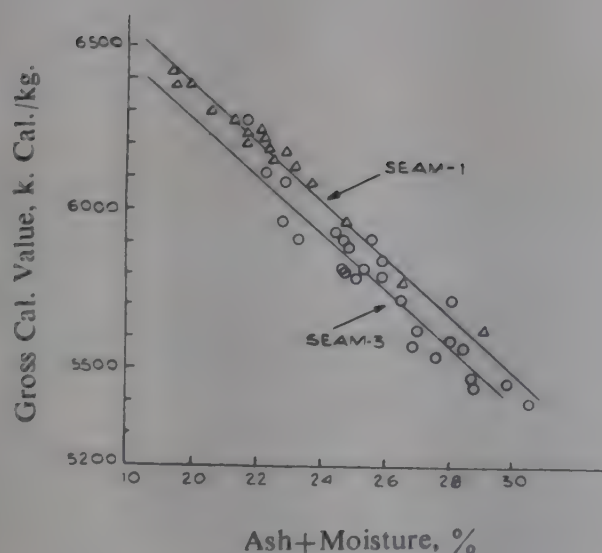


Fig. 3—Ash and Moisture vs Calorific Value in Ghordewa Sector Coal.

like initial deformation, softening and flow temperatures, in the fusion of ash were determined under a mildly reducing atmosphere simulating the gasifier condition. The ash pellets were placed on a platinum plate instead on a ceramic one and heated in the Lietz's apparatus⁸. The results are given in Table 3. The analysis of ash content of some of the coals are given in Table 4.

As in the cases of Talcher and Ramagundam projects,^{9, 10} it was observed that on screening the r.o.m. coals at 25 mm. the lump coals record a slight improvement in quality. Two r.o.m. coals from Surakachhar and one from Banki had been subjected to the screening test on 25 mm. (Table 5).

Results and Discussion

From the working area so far developed in the Surakachhar and Banki collieries, the properties of r.o.m. coal are as follows: it is sub-hydrous in nature; the moisture content of the air-dried samples

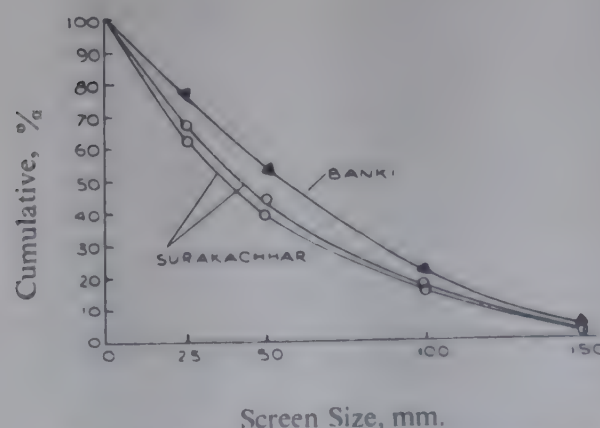


Fig. 4—Sieve Analysis of Run-of-mine Coal.

TABLE 1—ANALYSIS OF COAL SAMPLES, %
(Proximate analysis & Hardgrove index)

Sample No	Air Dry Basis (—72 mesh)				Dry Basis			D.a.f. Basis		Hardgrove Grindability Index
	Moist.	Ash	V.M.	F.C.	Ash	V.M.	F.C	V.M.	F.C.	
A: Surakachhar Coal										
PD/SUR- 1	7.5	17.2	24.1	51.2	18.6	26.1	55.3	32.0	68.0	48
PD/SUR- 2	7.5	20.9	24.5	47.1	22.6	26.5	50.9	34.2	65.8	55
PD/SUR- 3	5.6	17.2	25.1	52.1	18.2	26.6	55.2	32.5	67.5	53
PD/SUR- 4	6.0	18.6	25.1	50.3	19.3	26.7	53.5	33.3	66.7	53
PD/SUR- 5	6.5	19.2	23.5	50.8	20.5	25.1	54.4	31.6	68.4	57
PO/SUR- 6	5.1	21.9	24.4	48.6	23.1	25.7	51.2	33.4	66.6	51
PD/SUR- 7	7.2	18.0	24.1	50.7	19.4	26.0	54.6	32.2	67.8	50
PD/SUR- 8	7.5	20.4	24.0	48.1	22.1	25.9	52.0	33.3	66.7	51
PD/SUR- 9	7.6	19.2	24.2	49.0	20.8	26.2	53.0	33.1	66.9	56
PD/SUR-10	8.1	17.4	24.8	49.7	18.9	27.0	54.1	33.3	66.7	61
PD/SUR-11	7.2	25.7	23.0	44.1	27.7	24.7	47.5	34.2	65.8	57
PD/SUR-12	7.5	22.2	23.1	47.2	24.0	24.9	51.1	32.9	67.1	—
PD/SUR-13	8.0	17.8	24.2	50.0	19.3	26.3	54.4	32.6	67.4	—
PD/SUR-14	7.7	13.4	24.9	54.0	14.5	27.0	58.5	31.6	68.4	50
PD/SUR-15	6.9	15.3	24.7	53.1	16.4	26.6	57.0	31.7	68.3	45
B: Banki Coal										
PD/BNK- 2	6.7	21.9	22.5	48.9	23.5	24.1	52.4	31.5	68.5	53
PD/BNK- 3	8.3	15.4	23.8	52.5	16.8	25.4	57.3	31.2	68.8	52
PD/BNK- 4	8.3	18.0	24.4	49.3	19.6	26.6	53.8	33.1	66.9	50
PD/BNK- 5	7.4	17.8	24.7	50.1	19.2	26.6	54.2	33.0	67.0	53
PD/BNK- 6	8.0	18.3	23.7	50.0	20.0	25.7	54.3	32.2	67.8	55
PD/BNK- 7	7.5	19.9	24.1	48.5	21.5	26.1	52.4	33.2	66.8	53
PD/BNK- 8	7.9	19.0	23.6	49.5	20.6	25.6	53.8	32.3	67.7	57
PD/BNK- 9	7.8	20.9	24.1	47.2	22.7	26.1	51.2	33.8	66.2	58
PD/BNK-10	7.7	19.8	24.4	48.1	21.5	26.4	52.1	33.6	66.4	55
PD/BNK-11	7.9	16.5	25.0	50.6	17.9	27.1	55.0	33.0	67.0	—
PD/BNK-12	7.1	17.5	24.6	50.8	18.8	26.5	54.7	32.6	67.4	50

*Sample *Nos. PD—SuR-14 & 15 and PD/BNK-12 are seam samples.

range from 5.6 to 8.3 per cent—the average being 7.2. A seasonal variation of 2.0 per cent was observed on the same samples depending on temperature and relative humidity. The water content may be entirely different on a freshly mined coal due to the percolation of water resulting an increase of 3.5 per cent of moisture. A variation of ash from 17.2 to as high as 25.7 per cent was observed. As against this, the three channel samples showed 13.4, 15.3 and 17.5 per cent ash. The average ash contents of r.o.m. coal for both the collieries are 19.5 per cent, which on dry basis comes to 21.0 per cent. The volatile matter, unlike its rank, is low and ranges from 22.3 to 25.1 per cent on air-dry basis, their average being 24.1 per cent. The coal is non-caking (caking index < 5).

Hardgrove grindability index had a variation of 48 to 61, the average being 54. In this comparison, the three channel samples indicated lesser HGI. The gross calorific value of the air-dried samples was in the range 5500-6000 K.cal/kg. corresponding to ash

variation from 17 to 22 per cent. The net calorific value will be about 180 unit less than the gross one. A fair relationship of gross cal. val. with ash and moisture is given in Fig 3. The G-I seam coal possibly being at higher depth showed slightly higher calorific value than the G-III seam.

The organic nature of coal of this coalfield is characterized by low carbon and hydrogen—their normal range being 81-82 and 4.7—5.0 per cent on d.a.f. basis respectively. The sulphur content is normally below 0.6 per cent and phosphorus in traces.

The composition of coal ash (Table 4) showed a wide variation in respect to ferric oxide, which being a fluxing agent lower the fusion temperature of ash. The silica and alumina (with titania) content on ferric oxide-free basis showed a marked uniformity, viz., 68-69 and 28-29 per cent respectively. Alumina content was fairly high and lime (CaO) very low which makes the ash highly refractory. In order to bring

TABLE 2—ULTIMATE ANALYSIS AND CALORIFIC VALUE

Sample No.	Moisture, %	Ash, %	Ultimate Analysis (air-dry basis), %					Gross Calorific Value, K. cal/kg.		
			Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen by Diff.	Air-Dry Basis	Dry Basis	D.a.f. Basis.
1	2	3	4	5	6	7	8	9	10	11
PD/SUR- 1	7.5	17.2	62.62 (83.16)	3.66 (4.84)	0.31 (0.34)	1.24 (1.65)	7.47 (10.01)	5800	6270	7710
PD/SUR- 2	7.5	20.9	59.33 (82.87)	3.41 (4.71)	0.55 (0.60)	1.29 (1.70)	7.02 (10.12)	5560	6010	7770
PD/SUR- 3	5.6	17.2	63.00 (81.75)	3.53 (4.58)	0.63 (0.67)	1.29 (1.67)	8.75 (11.33)	6080	6440	7870
PD/SUR- 4	6.0	18.6	60.23 (79.87)	3.65 (4.76)	0.55 (0.59)	1.27 (1.69)	9.70 (13.09)	5810	6180	7710
PD/SUR- 5	6.5	19.2	61.35 (82.56)	3.65 (4.80)	0.55 (0.59)	1.25 (1.68)	7.50 (10.37)	5840	6230	7840
PD/SUR- 6	6.1	21.9	58.66 (81.49)	3.70 (5.14)	0.45 (0.48)	1.23 (1.71)	7.96 (11.18)	5710	6010	7820
PD/SUR- 7	6.8	18.0	60.59 (80.58)	3.73 (4.96)	0.53 (0.57)	1.25 (1.66)	9.10 (12.23)	5880	6330	7870
PD/SUR- 8	7.5	20.4	59.37 (82.35)	3.72 (5.16)	0.42 (0.45)	1.23 (1.70)	7.36 (10.34)	5580	6030	7730
PD/SUR- 9	7.6	19.2	58.87 (80.37)	3.78 (5.16)	0.52 (0.56)	1.23 (1.68)	8.80 (12.23)	5570	6030	7890
PD/SUR-10	8.1	17.4	59.36 (81.10)	3.57 (4.78)	0.46 (0.50)	1.28 (1.72)	9.83 (11.90)	5900	6420	7910
PD/SUR-11	7.2	25.7	53.81 (80.23)	3.35 (5.00)	0.40 (0.43)	1.11 (1.66)	8.43 (12.68)	5270	5680	7860
PD/SUR-12	7.5	22.2	57.06 (81.17)	3.24 (4.61)	0.49 (0.53)	1.22 (1.73)	8.29 (11.96)	5450	5890	7760
PD/SUR-13	8.0	17.8	60.52 (81.66)	3.56 (4.78)	0.46 (0.50)	1.22 (1.65)	8.44 (11.41)	5790	6290	7800
PD/SUR-14	7.7	13.4	64.69 (81.98)	3.68 (4.61)	0.23 (0.25)	1.34 (1.70)	8.96 (11.46)	6270	6790	7940
PD/SUR-15	6.9	15.3	62.30 (80.07)	3.54 (4.55)	0.45 (0.49)	1.31 (1.69)	10.20 (13.20)	6110	6560	7850
PD/BNK- 1	6.5	23.7	56.70 (81.23)	3.48 (4.99)	0.35 (0.37)	1.21 (1.74)	8.06 (11.67)	5390	5770	7720
PD/BNK- 2	6.7	21.9	57.84 (81.00)	3.43 (4.80)	0.26 (0.28)	1.19 (1.66)	8.68 (12.26)	5470	5860	7660
PD/BNK- 3	7.3	15.4	63.50 (82.15)	3.47 (4.49)	0.54 (0.58)	1.33 (1.71)	8.46 (11.07)	5960	6430	7720
PD/BNK- 4	7.2	18.0	61.73 (82.52)	3.30 (4.52)	0.65 (0.70)	1.26 (1.68)	7.86 (10.58)	5810	6260	7770
PD/BNK- 5	5.4	17.8	62.32 (81.14)	4.18 (5.44)	0.40 (0.42)	1.31 (1.70)	8.59 (11.30)	5900	6370	7880
PD/BNK- 6	6.7	18.3	61.03 (81.36)	4.09 (5.45)	0.47 (0.50)	1.24 (1.65)	8.17 (11.04)	5780	6280	7850
PD/BNK- 7	6.5	19.9	61.20 (81.20)	3.91 (5.32)	0.37 (0.40)	1.23 (1.67)	6.89 (11.41)	5710	6170	7850
PD/BNK- 8	7.9	19.0	59.65 (81.60)	3.68 (5.04)	0.68 (0.74)	1.26 (1.73)	7.83 (10.89)	5620	6100	7680
PD/BNK- 9	7.8	20.9	57.85 (81.14)	3.51 (4.93)	0.61 (0.66)	1.23 (1.72)	8.10 (11.55)	5440	5900	7630
PD/BNK-10	7.7	19.8	58.02 (80.04)	3.52 (4.85)	0.53 (0.57)	1.23 (1.70)	9.20 (12.84)	5540	6000	7640
PD/BNK-11	7.9	16.5	61.30 (81.08)	3.62 (4.79)	0.44 (0.48)	1.29 (1.71)	8.95 (11.94)	5920	6420	7850
PD/BNK-12	7.1	17.5	62.49 (81.55)	3.52 (4.73)	0.32 (0.35)	1.26 (1.70)	7.81 (11.67)	5900	6350	7830

Figures in parenthesis refer to analysis on d.a.f. basis.

TABLE 3—FUSION TEMPERATURE OF ASH OF COAL SAMPLES, °C

Sample No.	Ash Fusion Temperature under Mild Reducing Atmosphere		
	Initial Deformation Temp.	Softening Temp.	Flow Temp.
PD/SUR-1	1250	1310	1400
PD SUR-2	1245	1400	>1450
PD SUR-3	1300	>1450	>1450
PD SUR-4	1270	>1450	>1450
PD SUR-5	1280	>1450	>1450
PD SUR-6	1380	>1450	>1450
PD SUR-7	1320	>1450	>1450
PD SUR-8	1310	>1450	>1450
PD SUR-9	1290	1450	>1450
PD SUR-10	1330	>1450	>1450
PD SUR-11	1170	>1450	>1450
PD SUR-12	1270	1440	>1450
PD SUR-13	1260	1410	>1450
PD SUR-14	1370	>1450	>1450
PD SUR-15	1335	>1450	>1450
PD BNK-1	1215	1410	>1450
PD BNK-2	1250	1445	>1450
PD BNK-3	1300	>1450	>1450
PD/BNK-4	1280	>1450	>1450
PD BNK-5	1330	>1450	>1450
PD BNK-6	1280	1440	>1450
PD/BNK-7	1280	>1450	>1450
PD BNK-8	1300	1450	>1450
PD BNK-9	1250	1450	>1450
PD BNK-10	1310	1450	>1450
PD/BNK-11	1230	1420	>1450
PD/BNK-12	1270	1400	>1450

down the fusion temperature, it is necessary to add limestone to these coals. Where ferric oxide content is low addition of both lime and ferric oxide might be more effective.^{11, 12}

For a fertilizer plant, the raw material for the gasification part should be consistent in respect to ash content and ash quality. Coal being a natural product its ash content is not likely to be uniform. A screening test has been conducted to assess the distribution of ash in the fine and lump coal. The results on a Surakachher r.o.m. coal (Table 5) showed a difference of 2.6 per cent of ash between the +25 and -25 mm. fractions. The same test on Banki coal showed a wider variation. Since the gasification plant will require coal of a more consistent ash content and quality and the steam generation plant will tolerate a wider variation, and also the fact that the consumption of coal for gasification and steam generation would be in the ratio of 2:1, screening of r.o.m. coal on 25 mm. would be helpful for the project.

A number of borehole analyses were collected from the area which would be covered by the fertilizer factory and their ash content was noted. Assuming that the shale bands might not be properly re-

TABLE 4—ANALYSIS OF COAL ASH SAMPLES

Sample No.	SiO ₂ , %	Al ₂ O ₃ +TiO ₂ , %	Fe ₂ O ₃ , %	CaO %	MgO, %	SO ₃	Alkalis (by diff.)
PD/SUR- 2	61.08	24.80	11.70	0.91	0.36	1.37	0.48
PD/SUR- 5	61.65	25.20	10.00	0.95	0.58	0.79	0.83
PD/SUR-10	63.75	25.87	7.60	0.94	0.42	0.70	0.72
PD/SUR-15	60.88	27.45	7.20	0.91	0.72	1.51	1.33
PD/BNK- 2	62.72	25.25	8.80	0.98	0.86	0.69	0.70
PD/BNK- 3	59.55	24.93	11.90	1.12	1.24	0.33	0.93
PD/BNK- 8	61.10	24.97	10.80	0.89	0.80	0.49	0.95
PD/BNK-12	54.60	22.70	20.00	0.56	0.72	0.69	0.73

TABLE 5—ANALYSIS OF SCREENED R.O.M. COAL

Colliery	Particulars	Wt., %	Moist., %	Ash, %	V.M., %	F.C., %
Surakachhar Colliery	+25 mm., lump Coal	66.6	7.6	16.1	25.2	51.1
	-25 mm., Slack Coal	33.4	8.1	18.7	23.5	49.7
	R.O.M.					
	Overall	100.0	7.8	17.0	24.6	50.6
Banki Colliery	+25 mm. lump Coal	75.0	7.6	14.5	24.6	53.3
	-25 mm., Slack Coal	25.0	6.3	23.0	23.9	46.8
	R.O.M.					
	Overall	100.0	7.3	16.6	24.4	51.7

moved in the mining operation, the maximum possibility of ash content in these borehole samples has been calculated and differences tabulated (Table 6). Sufficient borehole data was not available for the area beyond the future 10 years' working by the CMA. It can be observed (Table 6) that on inclusion of shale bands ash percentage increased by 1-2 units.

From the borehole analysis of samples near the present position of mining, (Table 7) it can be seen that the average ash of r.o.m. coal is about 1.4 per cent higher than that of borehole analysis with bands.

TABLE 6—BOREHOLE ANALYSIS OF ASH AT SURAKACHHAR UNDER 1ST & 2ND 5 YEARS WORKING PLANS OF M/S. COAL MINING AUTHORITY LTD.

Borehole No.	Ash (air-dry basis without band), %		Ash (air-dry basis ; including bands), %	
	Seam I	Seam III	Seam I	Seam III
A : First 5 Years				
56	18.1	14.0	23.7	14.0
27	19.2	17.5	23.3	19.0
20	—	14.2	—	17.2
212	19.0	—	24.9	—
21	13.9	21.4	13.9	21.8
210	18.9	17.2	18.9	17.2
101	18.5	17.4	19.3	20.0
107	15.9	14.7	15.9	15.7
110	16.9	15.7	22.1	16.4
206	26.5	21.4	27.8	25.4
207	22.1	16.5	27.7	18.1
209	22.5	17.4	27.1	17.4
103	24.6	12.3	25.2	12.3
203	19.0	19.3	22.6	19.3
204	19.1	16.7	22.5	16.7
Average of Seams I & III	19.6	16.8	22.5	17.9
	18.2		20.2	
B : Second 5 Years				
213	—	15.1	—	15.1
259	—	24.0	—	26.1
199	18.6	17.5	21.1	17.5
200	19.3	20.6	22.0	20.6
181	17.8	18.0	21.0	18.0
182	20.1	16.1	23.0	16.1
184	17.4	14.8	17.4	14.8
151	17.3	—	20.0	—
152	23.8	16.3	23.8	16.3
Average of Seams I & III	19.2	17.8	21.2	18.1
	18.4		19.5	

TABLE 7—BOREHOLE ANALYSIS NEAR THE PRESENT MINING AREA AT SURAKACHHAR

Borehole No.	Ash (air-dry basis) G-III Seam, %	
	Without Band	With Band
110	15.7	16.4
206	21.4	25.4
209	17.4	17.4
107	14.7	15.7
103	12.3	12.3
101	17.4	20.0
210	17.2	17.2
21	21.4	21.8
Average	17.2	18.2

Conclusion

The availability of sufficient coal of uniform characteristics at Korba will be highly advantageous for operation of the coal-based fertilizer project, because of the availability of coal on the spot. It would be reasonable to expect a likely variation of ash (on dry basis) from 18 to 23 per cent from Surakachhar colliery which alone would supply 90 per cent of the coal requirement of the entire project. In general, the coal ash is slightly refractory and fluxing agents may be required to lower the fusion temperature for smooth operation of the gasification plant. Further work in this line is in progress.

Acknowledgement

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Technical Digests

Development of Iron Oxide-Based Desulphurization Masses for Gas Purification

In the dry gas purification process, imported varieties of oxide masses, such as luxmasse, bog iron ore, Monox oxide, etc., are still widely used for removal of hydrogen sulphide. In this laboratory, attempts were made to develop suitable substitutes of these materials to meet the specific requirements of different industrial users. Continuous and concerted research efforts in this direction have led to the successful development of iron oxide-based desulphurization masses (given below) of different grades highly suitable for removal of hydrogen sulphide from industrial gases. The purifying masses have remarkable hydrogen sulphide absorption power and regenerability. The products have been successfully used in various commercial plants. The indigenous production of these materials will be of immense potential value for gas purification and save this country an appreciable amount of foreign exchange.

(1) *Substitute of German Luxmasse*: An highly active iron oxide desulphurization mass has been developed for removal of hydrogen sulphide from Winkler gas under a pressure of about 14.5 kg./cm². The performance of this material was rigorously tested in a pilot test unit, installed in the fertilizer plant at Neyveli, under actual plant operating conditions. The pilot test results were very encouraging. In view of this, the material based on our developed formulation and process was manufactured and supplied to Neyveli Lignite Corporation. It was charged

in their gas purification unit during April-May 1974, where it has been giving encouraging performance.

- (i) Material supplied to Neyveli Lignite Corporation Ltd. Neyveli, Tamil Nadu—Qty. 60 MT
- (ii) Value of material—Rs. 2.10 lakhs.
- (iii) Estimated saving in foreign exchange on account of above production—about Rs. 2.10 lakhs.

(2) *Substitute of Japanese Nissan N-IND Mass*: A desulphurization iron oxide mass in extruded form has been developed for removal of hydrogen sulphide from carbon dioxide meant for urea manufacture. The chemical and physical characteristics of this material are similar to those of Japanese Nissan N-IND mass. Its performance results obtained during different trial tests under actual plant operating conditions at Gorakhpur were found highly encouraging and compared favourably with those of the imported mass presently used. This material was, therefore, prepared and supplied to the Gorakhpur Unit of FCI, where it was charged in the dry box during the first week of December, 1974. Its performance has been encouraging, and the Gorakhpur Unit has placed another order for 70 MT of this material.

- (i) Material supplied to Gorakhpur Unit of FCI Ltd.—70 MT.
- (ii) Value of material—About Rs. 4 lakhs.
- (iii) Estimated saving in foreign exchange on account of above production—About Rs. 4 lakhs.

(3) *Substitute of Imported Bog Ore*: An highly active hydrated fer-

ric oxide mass has been developed for complete removal of hydrogen sulphide from producer gas and fuel gases used for atmospheric control of the annealing plant furnaces. This material has been supplied to M/s. Indian Cable Co., Jamshedpur, for the last four years where it has been successfully used in place of imported bog ore. With the supply from this indigenously manufactured source the import of bog iron ore has completely stopped, as a result of which a considerable amount of foreign exchange has been saved.

- (i) Material supplied to M/s. Indian Cable Co., Jamshedpur (during Nov. 1971—June 1974)—103 MT
- (ii) Value of material—Rs. 4.12 lakhs.
- (iii) Estimated saving in foreign exchange on account of above—Rs. 4.12 lakhs.

(4) *Indigenous Substitute of Imported Manox Oxide*: An improved quality of ready-mixed desulphurization mass has been prepared from highly active hydrated iron oxide, wood shavings, additives, etc. for removal of hydrogen sulphide from fuel gases used for the atmosphere control of furnaces. This material has been supplied to M/s. Usha Martin Black (R/W), Ranchi, where it is giving excellent performance, much better than that of the imported Manox oxide used so far.

- (i) Material supplied to M/s. Usha Martin Black (R/W), Ranchi—3 MT.
- (ii) Value of material—Rs. 9,000/-.
- (iii) Estimated saving in foreign exchange on account of above production—About Rs. 9,000/-.

* Contributed by: A. C. Srivastava, L. D. Joshi, S. S. Gupta, P. K. Singh, D. D. Chatterjee and B. K. Dutta, P and D Division, FCI Ltd., Sindri.

Patents & Inventions, Etc.

Continuous Level Indicator For Solids and Liquids

This instrument, developed by the Instrumentation Department of the Planning & Development Division, Fertilizer Corporation of India Ltd. is under the first phase of manufacturing stage. Its complete know-how has already been sold to M/s Bestobell India Limited for its large-scale manufacture.

This continuous level indicator, based on the principle of capacitance, measures the level of solid or liquid material in a tank, hopper, bunker, vessel, etc. It basically measures the change in capacitance of the probe which occurs when the media (usually air) between the probe and the container is replaced by the solid or liquid of the container. This instrument displays this capacitance on a moving coil meter which is calibrated in percentage of metres. Thus, it indicates the solid or liquid level directly on the meter linearly.

This instrument consists of two parts one the wave generator-cum-detector fitted over the probe head and another the indicator located far-off in the control room. These two are connected by means of an ordinary three-core cable. The wave generator, which is fitted on the probe head, charges the probe capacitance which is formed between the central sensing electrode and the body of the container. When the positive half of the wave is applied, the said probe capacitance discharges through a resistor when the negative half of the cycle is applied there. This discharging current through a resistor is proportional to the value of the probe-capacitance. The more the value of the probe

capacitance, the higher is the current value through that resistor. We know well that the di-electric constant of a solid or liquid material is greater than that of air, therefore rising of the level of solid or liquid in a vessel around the vertical electrode increases the capacitance of the probe proportional to the level of the material in the vessel. Hence, the discharging current is proportional to the level in the container. This current is amplified and then transmitted to the indicator side, where it is displayed on a meter for visual indication.

Applications: It has a wide use in the industry for level measurement and control. It can be used for solid as well as liquid materials for continuous level measurement, and also in the refineries. It can be employed for materials, like powdered coal, cement, sugar, fertilizer, grains etc. as solid and water, urea slurries, acids, alkalis, etc. as liquid.

Special Features: (1) It employs 100% indigenous components; (2) the circuit is intrinsically safe and can be used for explosive services also; (3) an ordinary 3-core cable is used instead of a coaxial cable between the probe and the indicator; (4) induced voltage has no effect on the signal voltage transmitted to the indicator side; (5) it can be used for level measurements from $\frac{1}{2}$ meter to several metres of height; and (6) it has a linear scale.

Limitation: The exact length of the cable must be connected between the probe and the indicator prior to the adjustments for zero and full scale.

A Process for Reduction in Fluorine Content of Gypsum Cake*

The fluorine content of gypsum

cake, obtained as a by-product during the manufacture of phosphoric acid from rock phosphate as a result of the reaction of rock phosphate with sulphuric acid [$3\text{Ca}_3(\text{PO}_4)_2 + \text{CaF}_2 + 10\text{H}_2\text{SO}_4 + 20\text{H}_2\text{O} \longrightarrow 10\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 6\text{H}_3\text{PO}_4 + 2\text{HF}$], is reduced by washing the gypsum cake with solutions of ammonium sulphate. The by-product gypsum can be used for the manufacture of ammonium sulphate by the Merseburg process which involves its reaction with ammonium carbonate solution. The residue from such a reaction is used for the production of cement. The process of reduction of fluorine in gypsum, is illustrated by the example given below:

75 g of phosphate rock containing 36-37 per cent P_2O_5 , 48.98 per cent CaO , and 3.84 % F was treated with 240 ml. of aqueous H_3PO_4 solution containing 30% P_2O_5 and 85 ml. of aqueous H_2SO_4 solution containing 57% SO_3 at a temperature of 70°C for 4 hours. The resulting gypsum cake was separated and washed successively with 120 ml. of H_3PO_4 containing 14% P_2O_5 and 6 g of $(\text{NH}_4)_2\text{SO}_4$, with 120 ml. of H_3PO_4 containing 7% P_2O_5 and 3 g of $(\text{NH}_4)_2\text{SO}_4$, and with 120 ml. of distilled water. Then the gypsum cake was dried for 5 hours at 45°C . The fluorine content in the dried gypsum was 0.38% as compared with 0.54 and 1.02% F obtained by washing the cake with a solution containing 5g $(\text{NH}_4)_2\text{SO}_4$ /100 ml. of solution and with a solution without $(\text{NH}_4)_2\text{SO}_4$, respectively.

* Indian Pat No. 97990/5.2.65 (Inventor: K. R. Chakraverty, A. K. Roy, M. K. Bardhan and R. U. Singh)

Notes & News

Coal for Fertilizer Production in India's 6th Plan*

In the early years of industrialization, coal formed the basis for energy and chemicals production. The dominance of coal continued up to mid-fifties. The lignite-based fertilizer plant at Neyveli was also planned during this period. Between 1955 and 1964, there was a notable shift to liquid petroleum fuels consequent on the development of the partial oxidation process. Between 1964 and 1970, naphtha, for the first time, became an important feedstock for the production of chemicals and fertilizers. Another development during this period was the installation of large single train ammonia plants based largely on natural gas. Coal became progressively less important primarily due to its increasing cost on the one hand and easier availability of petroleum fuels on the other. However, in India, there continued a large demand for kerosene and diesel but not enough demand for naphtha for motor fuels. This resulted in the installation of a number of naphtha-based fertilizer plants in rapid succession between 1966 to 1972. This is evident from the fact that nearly 80% of the total installed capacity of about 2 million tonnes of nitrogen is based on naphtha.

The recent abnormal price hike on crude petroleum has once again called for our planners to reassess and identify the magnitude of our dependence on the use of petroleum feedstocks in fertilizer industry. India's economy is vitally dependent on adequate and timely supply of fertilizers. In the present state, it appears certain that coal would play a major role as a source of our fuel needs, both liquid and gaseous in replacement of petroleum sources. Thus, there are hardly any options left for India but to substitute the petroleum fuels as far as possible in the quickest possible time with coal whose resources are fortunately adequate. Despite urgency, India might have to depend, for a short term, on petroleum feedstocks for chemical fertilizer production to meet our needs. India's plans would require 10-12 million tonnes of nitrogen fertilizers by 1980-82 in

order to achieve a foodgrain production of the order of 180-200 million tonnes from the present level of 100-110 millions. Organic wastes, better water management and more efficient use of chemical fertilizers are the additional essential steps which will help in augmenting and attaining this food production target

Planning for the 6th Plan: In addition to the plants that are contemplated in the Fifth Plan, based on fuel oil, an additional 5 million tonnes of nitrogen production has to be planned for the Sixth Plan. This additional capacity could be achieved from 15 plants each of 1,500 tonnes per day ammonia capacity, which should have to be derived exclusively from coal. The success of such a massive programme would require advance planning to be taken up from early 1975 by a competent group of technologists in respect of location, investment, coal availability, cooling water facility and power needs for the individual fertilizer complexes. Such a complex would require more than 2 million tonnes of coal per year. Specifications in regards to plant and machinery, critical raw materials, piping and pipe fittings have to be outlined and advance action has to be initiated by the fabrication industry to make arrangement of these deliveries between 1978 and 1981. Judicious advance planning would also be necessary for making available such a huge investment of about Rs. 3,000 crores, Rs. 800-900 crores of which would be in foreign exchange.

World Nitrogen Outlook: Despite a massive increase in the world nitrogen production, the current shortage in the world nitrogen supply would continue, thereby hardening the prices still more. The industry is expanding substantially and the world capacity might increase to 117 million tonnes by 1980 provided the additional proposals also materialize. But the world distribution system looks distorted, and reviewing the overall situation of supply outstripping demand, imported fertilizers would cost Rs. 6,000 per tonne of nitrogen to India. This will enhance the import bill sharply and it would become beyond India's capacity to pay for fulfilling her requirements. Import of 5 million tonnes of nitrogen each year would require Rs. 3,000 crores in foreign exchange which does not look feasible in the foreseeable future.

Therefore, there is no option but to launch upon a massive programme of the type mentioned above.

Coal Resources & Development: The 5 million tonnes of nitrogen programme would require more than 30 million tonnes of coal. Coal resources should, therefore, be developed for these 15 units, which can be best done by identifying 11 new locations in addition to the expansion of the 4 already identified locations. This programme would call for an upward revision of the target of 200 million tonnes of coal in the sixth plan to accommodate the requirement of this proposed fertilizer programme. The coal and lignite reserves of India are currently estimated at 83,000 million tonnes, of which nearly 75 per cent is non-coking coal. A non-coking coal quality upto 28% ash plus moisture should form the basis for the fertilizer programme.

Current Status of Coal Technology and R & D Efforts: USA is currently investing a lot on the R & D efforts to develop suitable technologies for production of clean fuels from coal. The Union Carbide has developed a fluid-bed process with circulating hot ash agglomerates for supplying heat for endothermic steam-carbon reactions, thus eliminating the need for external oxygen. Union Carbide is currently engineering a pilot plant at Bhopal (M.P.), based on the experiences of a 25 tpd plant at Battelle (USA) for 150 tpd throughout. The Indian plant would establish the suitability of Indian coals and provide design data for commercial scale plants. National Committee on science & Technology has agreed to the construction of a demonstration plant by FCI Ltd. on the hydrogasification process route and plans are being formulated to progress the work. However, current studies on R & D efforts in these fields indicate that none of the promising ones would be developed to an extent for commercial application. Therefore, the choice of technology for commercial plant installation would have to be restricted to the reliable technologies available today for such purpose. The experts in a recent international seminar in April 1974 at Delhi concluded that it would be advantageous to proceed with proven technologies rather than wait and anticipate improvements from current R & D efforts and possible outcome of newer technologies.

* Based on a speech delivered by Dr. S. K. Mukherjee, Director F.C.I. Ltd., at a meeting of the Indian Chemical Manufacturers' Association at Calcutta on Sept. 24, 1974

Coal Based Developments in India*

It is well known that the natural resources of a country help largely in building up the socio-economic structure of its people. For self-reliance, a country must concentrate its efforts and adopt technology suiting to its own prime resources. In this context, the most important natural resource which could lead to self-reliant development in our country is the vast deposits of coal which can form the prime source for the ever-expanding requirements of energy for our growing population as well as a pivotal point around which industrial socio-economic activity could be built.

The development of our economy has till now placed too much reliance on crude oil and its derivatives and as such some 65-70% of the crude has to be imported. The difficult situation arisen by the indiscriminate licensing of fertilizer plants based on naphtha is now known to every body. In many cases convenience and unrealistic pricing policies, though these are against overall national interest, have encouraged the use of fuel oil in place of coal. The use of coal and its by-products, like tar and coke-oven gas, which can serve as starting materials for manufacturing organic chemicals, has been completely overlooked and neglected. The country's interest would have been best served had dependence on oil derivatives been confined to the role of a supplement to tar or coal derivatives or to cover such cases where the latter are technically unsuitable. We should take the exemplary lessons from the pre-war Germany, who developed the technology for coal and lignite conversion to oil products. Bergius process for coal hydrogenation and the Fischer-Tropsch synthesis for hydrogenation of carbon monoxide to yield a wide variety of hydrocarbons are all the brain children of the German innovators wedded to the creed of self-reliance. Another present day example of a nation which took seriously to build its economy on domestic sources wedded to adaptive technology is the Union of South Africa, who with its poor oil resources and abundant coal reserves had set out to manufacture its fertilizer, chemicals and liquid or gaseous fuels using coal as raw material. All these examples are there for us showing the pitfalls which we should avoid in planning our industrial growth, if only we would have the wisdom to follow these seriously enough.

* H. K. Sen Memorial Lecture 1973 delivered by Dr. K. R. Chakravorty, Formerly Managing Director, FCI Ltd. New Delhi, on Sept. 20, 1974 at Calcutta.

In the context of the present international oil crisis and exorbitant prices of crude and naphtha, our country must review the position as to how it would keep the naphtha-based fertilizer plants supplied with the feedstock and also to try all means to get a sufficient amount of naphtha released from its use as gasoline in automobiles by suitably substituting with alternate fuel which can be produced indigenously. The logical advocacy of a suitable feedstock by the Planning & Development Division of the FCI Ltd. has resulted the acceptance of establishing three of its coal-based fertilizer projects; one at Ramagundam (Andhra Pradesh), another at Talcher (Orissa) and the revival of the once-abandoned Korba project in Madhya Pradesh. Serious thought is also being given now to the addition to this list of coal-based plants.

But then the consequences of erroneous choices made in the past are still with us and the fate of the 20 naphtha-based installations (some of which are under construction) is still causing concern as to where from the required feedstock would come. In such an event, the technology of deriving synthetic liquid hydrocarbon by coal hydrogenation, though complicated, should become our automatic choice. Such plants would, no doubt, require considerable capital. Besides this, the other processes, like Fischer-Tropsch synthesis and hydrogenation of LTC tar, etc., can also offer very promising solution for our country. A low temperature carbonization plant has an additional benefit, viz. the soft coke which can reduce kerosene consumption in a big way.

Another way would be to produce methanol from coal in large quantities. Methanol can blend in limited proportions with naphtha for use as a motor car fuel, thereby release corresponding amounts of naphtha for feeding fertilizer plants. In fact, it may even be able to substitute naphtha as a light vehicle fuel provided the engines are specifically adjusted for its use. The possibility of blending of methanol with naphtha has been mentioned in the literature. This would, however, require all-out efforts to be made to overcome the difficulty of blending so as to get a uniform mixture which can substitute for the motor spirit. Above all, the actual production cost of methanol from coal-based operations has been worked out to be Rs. 800/te (assuming the coal price, Rs. 56/te), whereas methanol's price in the international market was about Rs. 1,800/te in February, 1974. Furthermore, there seems to be a considerably good trade of this commodity in the international arena. It would, therefore, be a good idea

to earmark part of coal based-methanol for export and to the extent a margin of profit can be made on the same, subsidizing its issue price to domestic fertilizer manufacturers. Methanol has the potentialities to be used as a source of hydrogen or reducing gases, not only for fertilizer manufacture, but also for other chemical application. It can be split back into CO and H₂ by catalytic cracking at very moderate temperatures. While examining the economics of the cost of manufacturing it from naphtha, (price Rs. 1,000/te) it is found that methanol (using the low pressure loop and centrifugal compression, etc.) would cost Rs. 1,300/te. On the other hand, its price, even if the coal prices rise from the base figure of Rs. 56-100/te would be in a better competitive position in the foreseeable future, if manufactured from coal.

The current consumption of naphtha in our country is estimated about 1.6 million tonnes/year which is likely to rise to 2.2 millions by 1978-79. If a 30% blend with methanol is made, it would be possible to release 480,000 tonnes of naphtha to fertilizer and allied industries. By cutting our wasteful use of naphtha as a fuel, most of this surplus material from refineries could be earmarked as an industrial feedstock. Efforts could also be made to develop a car engine which will exclusively use methanol as a fuel. The use of methanol as a motor fuel could also minimize significantly the pollution problem of motor car exhaust. The low profitability (5-10%) of a fertilizer factory could show an upward trend (18-25%) by combining the production of methanol with nitrogenous fertilizers, depending on the higher price fixed for urea as compared to the present level.

The present situation created by the international oil crisis, which forced the Union Govt. to increase the price of naphtha initially from Rs. 446 to Rs. 2,320/te, would result an increase of 75 to 300% in the price of large number of naphtha-based primary products. Even though the price of naphtha has now been fixed at Rs. 1,000/te for petrochemical production there has been upward refixation of its price for fertilizer production. This clearly brings to the surface the invalidity of the very basis of economic justification of installing these plants based on naphtha ignoring the indigenous raw materials like coke oven gas and tar products which are, at present, being burnt in furnaces and from which these very chemicals could have been conveniently manufactured.

Two important starting materials from which petrochemical products could be manufactured are ethylene

fraction of coke oven gas and acetylene derived from pyrolysis of methanol content of coke oven gas (in addition to ethyl alcohol from sugar factories). Acetylene-based products can be manufactured by pyrolysis of methane from coke oven gas. This gas, produced from coal, can replace a petroleum-based feedstock, like naphtha, for manufacture of acetylene/ethylene-based compounds. In relevant locations, hydrogen fraction and side products, such as acetylene off-gases, can be processed to manufacture ammonia and nitric acid which may be used for nitrophosphatic fertilizer manufacture. The basic chemicals like ethylene oxide, ethylene glycol, diethylene glycol, polyethylene glycol, ethylene dichloride and various amines, which are now obtained from naphtha-based petrochemical complex, could be prepared from ethylene fraction of coke oven gas.

Similarly, the acetylene route starting from the methane fraction of coke oven gas could give products, like chloroprene, neoprene, vinyl chloride, polyvinyl chloride, acetaldehyde and acetic acid, butanol, propanol, etc., which are now obtained from petrochemical complex based on naphtha. After making complete use of these coal-based products, the country should consider setting up of the plants based on naphtha to satisfy the unsatisfied demands seeing to the genuine needs. It is, therefore, very much urgent and necessary that a thorough review of fundamental approach to planning on these allied fields, viz. fertilizers and petrochemicals, be given a serious consideration.

Self-reliance does not only mean to utilize our own prime endowment, coal, but also to derive the maximum benefits in terms of socio-economic advancement. This idea looks well served by observing and assessing the additional employment potential. To mention an exemplary figure, a coal-based 2.5M.T. synthetic oil project generates additional employment potential of about 50,000 persons compared to a similar capacity plant based on imported crude. Although investment and running cost for coal-based plants are high, yet the national benefits have to be assessed in totality. While most of the costs in coal-based plants are assets to the nation, most of the costs for the plant based on imported crude are liability to the country.

Additional Refinery Capacities in the 5th Plan: The present dependence on imported oil calls our planners to critically examine any issue which comes up with a bearing on refining capacity fed on imported crude. But nagging doubts arise

when one hears of plans to expand refinery capacity in the country from 22 million to 37.2 million tonnes per year crude by 1978-79. Out of the present capacity of refining 22 million crude/year, hardly 7 to 8 million come from our indigenous sources. New discoveries as have been projected for Bombay High would at best marginally fill the gap between present capacity and domestic production. Oil yield from Bombay High project, when materialises, should only be utilized to meet the import gap for generating additional capacity. The import of crude will not only push up our import bill but also tie up a vast segment of our economy to imported prime resources. The recent oil crisis has given a shock to those, who in the past were advocating a *laissez faire* policy about our fuel and feedstock utilization patterns but are now convinced that they were fundamentally wrong in the approach for neglecting emphasis on coal as prime source for their needs. Sufficient efforts are required to be made to find out and establish possible alternate substitutes for many of the products based on indigenous resources as well as cutting down many sophisticated products which are not absolutely essential for the country. The idea of additional capacity, as envisaged, is to fill up the naphtha deficit, particularly created by indiscriminate licensing of naphtha-based installations. The demand for naphtha as industrial feedstock has been put at 4.2 million te/yr. Out of this, consumption of naphtha as fuel can be substituted by any other manufactured gas, thus saving naphtha to the extent. The major share of the petrochemical products could be based on coke oven gas and coal tar and from ethanol produced from sugar industry. A very serious question to our planners is: while projecting a demand for fuel oil for 5.9-12 million te/yr. in the Fifth plan has all possible steps to find indigenous substitutes to reduce the demand been considered? There would, no doubt, be difficulties of switching over to preparations at a short notice for want of high cost of development, import of technology and discomfort on operations due to lower calorific value. All measures leading to self-reliance demand a considerable amount of sacrifice on our part whether it be on a higher price to be paid, lesser speed and efficiency to be tolerated and so on. Top-most priority is required to be given to the new developments taking place in coal gasification programmes.

Coming back to coal-based projects, any expert knows that coal processing plants whether for manufacture of fertilizer or fertilizer-cum-methanol or other chemical products,

can not be located anywhere. Such a location must have a ready and assured offtake for fertilizer and other products, reliable and secure sources of utilities, like power, etc., and prices at reasonable rates. From these angles, coal-based developments must be located in the coal-bearing areas of Andhra, Assam, Bihar, M.P., Orissa, U.P. and West Bengal for rational development.

Oil from Coal by Fischer-Tropsch Process

The present world energy crisis and the price hike in petroleum crudes by oil exporting countries, has once again pressed us to reassess the techno-economics of the production of liquid fuels from coal. The Fischer-Tropsch process is one of the routes for conversion of coal to oil.

Status of Technology: In this process coal is first gasified to yield a mixture of carbon monoxide and hydrogen (synthesis gas). The gas is purified to remove carbon dioxide, sulphur components and other impurities. The synthesis gas is then catalytically converted to a mixture of hydrocarbons at 20-30 atmospheres and 200-320°C. The products of conversion are then processed further to yield the desired end-products, viz. LPG, naphtha, kerosene, diesel, etc.

Gasification: Both sized and dust coal can be gasified by known processes of pressure and dust coal gasification techniques respectively. Coal preparation is an important operation for all types of processes. When the pressure gasification technique is employed, coal is deshelled by crushing followed by screening. For pressure gasification plant with a capacity of one million tonnes per year of synthesis gas, 4.4 million tonnes per year of coal in the size range 40-8 mm would be required. The synthesis gas is produced by the reaction of steam and oxygen with carbon in the coal. The raw synthesis gas produced is freed from carbon dioxide and other compounds by either of the two schemes for purification.

(i) Hot Potassium Carbonate-Iron Oxide—Raw gas is first scrubbed with hot potassium carbonate solution to reduce the concentration of CO₂ in the gas to a desired level. The cooled gas is freed from H₂S in hydrogen sulphide towers containing moist ferric oxide. Part of the organic sulphur compounds are removed by adsorption over activated carbon.

(ii) Rectisol Process—This process, developed by Lurgi, involves absorption of impurities like carbon

dioxide, sulphur compound etc. in cold methanol under pressure. The complete removal of all impurities takes place in a single process unit comprising of three steps. Used methanol can be regenerated and recycled. This scheme enables synthesis gas to attain a very high degree of purity.

F.T. Catalysts: At the Central Fuel Research Institute, Dhanbad, the F.T. process has been studied using reduced and nitrided iron catalysts in bench and semi-pilot scale units. The nitrided iron catalysts are found to resist carbon deposition and have a longer life than the corresponding reduced catalysts. The normal life of 6-12 months of a catalyst in the fixed bed reactor can, however, be increased by washing the catalyst with a solvent at regular intervals of 4-5 months for removing higher boiling hydrocarbons from the surface.

Synthesis Reactors: F. T. reaction is highly exothermic, releasing 4,000 K cal/kg. of product formed. Out of the seven types of reactors developed so far, only two have attained commercial status. These two types, improved fixed bed and entrained fluid bed reactors, are successfully running at SASOL, South Africa, since 1955. The former known as Arge reactor has been developed and designed by Lurgi Ruhrchemie and the latter one by M. W. Kellogg Co. of U.S.A.

Products: The F. T. process is versatile and different types of products can be obtained by changing the process conditions and the catalyst. It has been observed that the fixed bed reactor produces more of higher boiling hydrocarbons and less of chemicals while the entrained bed reactor produces more of low boiling hydrocarbons and also more of chemicals. As the F. T. synthesis products are free from sulphur and nitrogen, therefore, these clean fuels can become excellent raw materials for their further processing into petro-chemicals.

Economy: Theoretically any coal can be gasified to produce gas for synthesis. But factors like caking property, nature of the mineral matter in coal and specially the inert content (ash and moisture) effect the cost of the coal preparation and also the yield of the gas.

The pressure gasification process involves deshelling of the r.o.m. coal with an inert content of 28-30% to produce a uniform coal feed in two size fractions of 40-10 mm, and less than 10 mm. using 40-10 mm. size for gasification and 10-0 mm. for production of power and steam ne-

cessary for the process. The raw gas from the gasifier is purified to remove the impurities, it is then mixed with a part of tail gas and methane is reformed. The synthesis gas with a H_2/CO ratio around two is sent to fixed bed reactors. The products mixed with unreacted feed are cooled, separated to various fractions are subjected to further processing.

While calculating the cost of production for plants with 1.0, 0.5 and 0.25 million tonnes capacities, it has been observed that any capacity below one million tonne products per year would not be economical under the present market prices. The return on investment for one million tonnes product per year is nearly 10 per cent which is quite considerable although not very high as in the case of petroleum refineries.

[S. Basu & V. A. Krishnamurthy, *Chem. Age India*, 25 (9) (1974), 633].

Installation of Gobar Gas Plant

The Gobar gas plant works on the simple principle that fermentation of dung or any other organic material in the absence of air, produces a combustible methane gas; the spent residue becomes available for use as manure.

Construction: A well, 2 metres in diameter, is dug to a depth of 4 metres. A sloping channel of 15 cm diameter is dug to a horizontal distance of 60 cm from the well carried to a depth of 65 cm above the bottom of the well. The bottom is then brick floored and plastered with cement. A well, one brick thick is now raised from the bottom, keeping an internal diameter of 1.35 metre of the well. The feeding pipe is then fixed in position in the channel and burried, with one end projecting 10 cm inside the well and other about 25 cm above ground level. Brick lining of the well is done to a depth of 1 metre from the top. The gas holder is supported on three brick cornices projecting 15 cm inside the well. A channel 10 cm wide is taken from the top for carrying the overflowing used slurry to the compost pit. A small brick lined pit, 30 cm square and 30 cm deep, just outside the well serves as a water catch to remove the condensed moisture from the gas pipe. The pipeline for the gas is kept clear by opening the top periodically say once a week. The gas outlet pipe with wheel cock is then connected with the pipeline taken to the kitchen where as suitable gas tap is fixed to take off gas for burning. The dung is then carefully introduced into the well so as to rest on the three projecting supports. Three 240 cm long black iron pipes 4.2 cm

in diameter, with pulleys on the top are fixed at equidistant points outside the well. Three iron buckets are tied to each of the handles of the gas drum. The wires are then passed over the pulleys so that the buckets keep hanging 45 cm from the ground level. The pipeline is fixed to one of the supporting pipes, with a bend at the upper end to which is attached one end of a 240 cm long hose pipe and the other end is connected to the nipple in the drum.

Operation: Cow Dung is first mad into a slurry with an equal proportion of water and introduced in the fermentation well through the funnel until it is completely full. This operation may take a week or more and require about 1,000 kg fresh dung to fill. The wheel cock of the gas holder should be kept open during this period to allow the air to escape. Production of the gas starts within a week, the gas accumulating inside the holder causing it to float and rise. The first portion of the gas after installation may not burn due to large proportions of carbon dioxide in it. In such cases the rubber hose is detached and the wheel cock opened to release the gas. The drum will settle down and again rise with fresh gas which may be similarly tested. After the gas has first formed, production is maintained by feeding about 50 kg of fresh dung slurry (with equal proportion of water) every day. This produces about 3 cubic metres of gas daily, sufficient for cooking requirements of an average sized family. An average sized gobar gas plant costs less than Rs. 1,000. Four or five animals can produce enough dung to run a small plant. Large sized gas plants can be constructed on the same principle by increasing the dimensions of the fermentation well. These bigger plants would need more dung.

Augumenting Yield of Gas: In the North, the yield of gas obtained in winter is reduced to about one-third due to the effect of low temperature on the activities of the microorganisms. About 1 kg powdered leaves or wheat straw mixed with 50 kg dung will give increased yield of gas. The gas plant may be covered with wood or polythene structure to maintain high temperature inside.

The gas is excellent for cooking purposes, since the blue and smokeless flame provides a neat and efficient fuel. The usual petrol, kerosene and diesel oil engines of any horse power can be adapted to run on gobar gas and the power generated utilised for pumping irrigation water, grinding flour, generating electricity, etc. For this purpose,

large capacity gas plants can be constructed.

[Krishnan Kumar, *Bombay Market*, Oct. 15 (1974), 89]

The Government of India proposes to instal 100,000 gobar gas plants, 300 sewage and sullage irrigation schemes and 2 mechanical compost plants. It will give 25 per cent subsidy towards the capital cost of gobar gas plants installed by farmers. The Centre has sanctioned Rs. 9 crores during the Fifth plan for the development and use of local manurial resources.

Process for Potassium Phosphates

Potassium phosphates were not used as fertilizer earlier because of the cost of manufacturing them. Recently however, a more economical new process has been developed by Pennzoil Chemical Inc., converting a phosphoric acid plant at Stanford Calif. USA to begin producing potassium phosphates during 1974.

Advantages of Potassium Phosphates as Fertilizers: The following are the advantages: (i) They possess a considerably higher concentration of P and K nutrients than the conventional materials; (ii) as they contain no chloride, potassium phosphates are ideal for use with chloride-sensitive crops such as tobacco or potatoes; they are compatible with ammonium nitrate; (iii) they have a low salt Index in comparison to most of the conventional fertilizers. The lower the salt Index of a fertilizer, the less it would tend to inhibit seed germination and sprouting or cause scorching.

Difficulties with the Existing Methods: The common method of obtaining potassium phosphates by

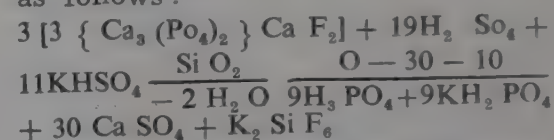
the reaction of phosphoric acid with caustic potash is much too expensive. Another method which attracts attention is the acidulation of potassium chloride with phosphoric acid. But this procedure has a number of disadvantages, as it requires elevated temperatures at which polymeric phosphates, rather than orthophosphate, are formed making the control of solubility difficult. Moisture is evolved as well as hydrogen chloride. Finally, the wet, impure HCl causes severe corrosion at the temperature involved.

New Process via Potassium Bisulphate: In an effort to overcome the difficulties associated with the KCl/H₃PO₄ acidulation process, a new process was developed by Goulding Fertilizers Ltd. of Dublin (Eire) in 1970, the patent rights of which were acquired by Pennzoil Co. of Houston, Texas. The basic process proceeds in the following manner: Potassium chloride is mixed with a proportional amount of concentrated sulphuric acid at about 125°C, when dry HCl is evolved leaving a slurry of potassium bisulphate in sulphuric acid. The slurry is then contacted with phosphate rock at about 70°C in a reactor to form monopotassium phosphate and gypsum. After separating the gypsum, the filtrate is a concentrated by evaporation and finally precipitated by adding methanol. The solid monopotassium phosphate is removed in a centrifuge, washed with more methanol and dried. The main features of this process are: (a) it separates the decomposition of the potassium chloride and the formation of the potassium phosphate takes place in two distinct stages, thereby allowing a lower temperature to be used

in the second and thus reducing the tendency of the potassium phosphate to polymerize; (b) the use of an excess of sulphuric acid in the decomposition of potassium chloride allows a lower temperature to be used in that stage. Also at the lower temperature (125°C), corrosion is much less severe.

The by-product hydrogen chloride is anhydrous and of high enough purity to be used in the production of chlorine or of organic-chloro compounds such as ethylene dichloride (EDC) a precursor of vinyl chloride. Alternatively, the HCl can be absorbed in water and used either to produce feed-grade dicalcium phosphate or in other industrial processes.

Reaction Involved: The overall reaction taking place in the rock acidulation stage may be summarized as follows:



As can be seen from the equation above, some potash loss, amounting to 18.2%, will also result from the formation of potassium fluosilicate. Pennzoil process, however, expects to recover 80-90% of the fluorides.

The primary potassium phosphate material produced in the process, fertilizer grade monobasic potassium phosphate KH₂PO₄, has an analysis of approximately 0-47-31 with a plant feed ratio of 0/3/2. However, the ideal plant nutrient ratio is about 0:5:4, which can be achieved by admixing a certain amount of dipotassium phosphate, K₂HPO₄, with the monopotassium salt to act as a polymer chain terminator.

News in Brief

SO₂ to Replace O₂ for Gasifying Coal Char

There are basically two methods of converting coal into substitute natural gas (SNG); by partial oxidation/steam gasification and by hydrogenation. Most of the large commercial coal gasification plants scheduled for construction in the next few years will be based on the partial oxidation/steam gasification method. In this method, a part of the coal is burnt in a deficiency of oxygen and heat so produced is needed to gasify the remainder with steam yielding mainly carbon monoxide and hydrogen; methane, however, is produced from this mixture in a subsequent stage. This would require pure oxygen which means that the gasification plant must have its own air separation plant as well.

Experimental work carried out on a gasification method at Babcock & Wilcox Research Centre at Alliance, Ohio (U.S.) suggests the use of SO₂ instead of O₂. Laboratory tests have shown that sulphur dioxide reacts with carbon at 1,200°C and space velocities of 700-800 per hr. to form elemental sulphur and carbon monoxide. When pure SO₂ is used, there is a tendency for carbonyl sulphide to be formed in large amounts, so rapid quenching in a fluidized bed to remove the elemental sulphur before it can react with the carbon monoxide is preferred. Sulphur dioxide for this reaction can either be recovered from waste gases by a regenerative scrubbing process or be produced by burning sulphur in air and then using such a scrubbing process to separate it from the nitrogen.

[*Sulphur*, 111 (March/April 1974), 55]

Credit to Sindri Fertilizer Factory

The World Bank announced on November 27, 1974 a credit of \$91 million (approx. Rs. 70 crores) from its soft-lending affiliate, IDA, for modernization and expansion of the Sindri fertilizer factory. The credit will assist the addition of a 900 tons/day ammonia plant and a 1,000 tons/day Urea plant. The project is likely to be completed in 1978.

Bio-Gas and Fertilizer From Farm Wastes

The National Sugar Institute has successfully carried out experiments for converting agricultural wastes into bio-gas and bio-fertilizer. Investigations conducted, so far, have revealed that 13-14 tonnes of agri-

cultural wastes comprising leaves, bagasse and grass can produce 2,400 cubic metres of bio-gas and 25-28 tonnes of moist bio-fertilizer. The fertilizer has been found to have better manuring qualities than farmyard manure or any other compost or organic fertilizer. The process for the preparation of bio-gas and bio-fertilizer from agricultural wastes consists of fermentation of the cellulosic plant residue in the presence of small quantities of nitrogenous and phosphatic nutrients. The mass is filled in m.s. cylindrical tanks with interposition of nutrients, like urea and animal dung. This dry mass comprising bagasse, leaves and grass is moistened with water or overflows from the previous charge to obtain a moisture content of 70 per cent. During irrigation, compressed air is blown as a result of which the mass gets impregnated with a mixed flora of micro-organisms which set in aerobic decomposition is allowed to continue for five days. The atmosphere is then made anaerobic in another two or three days the mass begins to yield gas which becomes richer and richer to methane content till its concentration rises to 55 per cent. The mass is allowed to decompose for another 60 days or so when the compost is ready and is taken out for use as manure.

[*Economic Trends*, 3 (24) (1974), 29]

Formaldehyde Titration for Determination of Ammoniacal Nitrogen in Phosphatic Fertilizers

According to AOAC (Official Method of Analysis, 1970 Association of Official Analytical Chemists, Washington, USA), the formaldehyde titration method is applicable to ammonium nitrate and ammonium sulphate samples. To make the method applicable to mixtures of diammonium phosphate and monoammonium phosphate, the sample solution is neutralized prior to addition of neutral formaldehyde, first to phenolphthalein end point and then adjusted to pH of the solution to 8.1. 10 millilitres of 1:1 formaldehyde neutralized to phenolphthalein end-point is added to the neutralized solution and it is set aside for 5 minutes. A pinch of sodium chloride is added and solution is titrated against a standard alkali using mixed screened indicator (the indicator is prepared by dissolving 0.1g methyl red plus 0.05 g methylene blue plus 0.1 g phenolphthalein in 150 ml. alcohol) to pinkish violet

end-point and finally finishing the titration to pH 9.7.

[TSR Anjaneyulu, *ISI Bulletin*, 26 (10) (1974), 386]

Seaweeds as a Source of Manure and Fodder

Seaweeds are used in agriculture as manure and fodder. The practice of manuring with seaweeds is prevalent in coastal areas particularly in Western Europe. *Fucus* and several species of *Laminaria* are collected from sea and used in horticulture. The composition, given below, of these two dry seaweeds, speak of their manuring quality.

(Per cent of air-dry weeds)

	Water-soluble Ash	Potash
<i>Laminarias</i>	16.9-28.6	4.5-11.9
<i>Fucus</i>	15.6-16.2	2.6- 3.8

(Tressler, Marine Products of Commerce, 1940, p. 74).

Meal made from dried *Laminaria* and *Ascophyllum* is used to improve crumbs and water-retaining quality of the soil. Seaweeds are also composted in various ways. Burning the weed and using the ash is an alternative practice in China where the ash is used as a fertilizer. Seaweed is found to be nearly as rich in nitrogen and organic matter as the farmyard manure; twice as rich in potash, poorer in phosphate and richer in common salt. Hence, good results are obtained when seaweed is combined with ammonium sulphate and superphosphate in the proportion of 15 tonnes of seaweeds to 50 kg of ammonium sulphate and 200 kg. of superphosphate to be used for each acre of land. Trace elements are also present. Seaweeds are also free from weed seeds that may introduce disease or impair the growth of crops.

Recovery of Potash From Distillery-Waste

The distillery-waste is a source of potash in the European countries as well as in USA, where large potash deposits occur. On the other hand, this waste water is always discharged into sewers in this country. India has a limited resource of potash available and her requirement is met with from imports. At present, there are sixty-two distilleries in India based on molasses which discharge about 5,000 million litres waste water every year. The

composition of this waste water varies from distillery to distillery due to variation in the quality of molasses but it contains 1.6 per cent potash always along with some amounts of floating and suspended solids, muds and putrescible organic matter. It has been seen possible to recover all potash from this waste-water with the help of solar energy and the Indian climate conditions are most ideal for it. After converting into light-brownish syrup with natural evaporation, this waste is burned to produce an ash which contains about 30-35 per cent potash depending upon the quantities of foreign matters like mud etc. The heat produced during burning the brownish liquid, might be utilized in enhancing the evaporation of waste-water. With complete utilization of the distillery-waste, it might be possible to produce 8,000 tonnes of potash annually in this country and to save foreign exchange. No doubt, this sunny and dry weather is highly suited to this operation, but can continue in other seasons also by little investment after study of the local meteorological conditions.

The proposed scheme is highly economical and feasible in Indian conditions and can operate easily by an unskilled labour. The problems relating to pollution, obnoxious smell etc. can be solved with little scientific management and precautions.

(B. S. Gupta, *Indian Chemical Society, Golden Jubilee No.*, 1973, p. 222).

Reserves of Oil & Gas in Bombay High

The Minister of State for Petroleum and Chemicals, Sri Shah Nawaz Khan, disclosed in the Parliament recently that the recoverable reserves of oil and gas as a result of exploratory drilling carried out so far in the Bombay High off-shore had been estimated at 108 mil. tonnes and 25,000 cu. mil. metres respectively. The Oil and Natural Gas Commission had also discovered 31 oil or gas bearing areas (25 in Gujarat and 6 in Assam).

[*Indian Engng. News Rec.*, 26 (Nov. 7) (1974), 1]

Compost Plant at Calcutta

The Ministry of Agriculture, Govt. of India, has recommended for sanction Rs. 60 lakhs for a mechanical compost plant at Calcutta, which will have a capacity of 150 tonnes/day of garbage. This organic manure contains about 5% nitrogen, 0.78% phosphate and 0.5% potash and other micronutrients.

[*Indian Engng. News, Rec.*, 26 (Nov. 7) (1974), 8]

Hydrogen As Basic Fuel

Prof. Vladimir Struminsky, a Lenin Prize winner Russian scientist, says that the world's energy problems can be solved if plentiful hydrogen gas are used as a basic fuel instead of hydrocarbons. Water is the most abundant source of the gas. Huge floating atomic stations in the oceans would produce hydrogen by splitting sea water and the gas could then be piped ashore for use in all branches of industry. As a cheap non-polluting fuel it could be used in normal petrol engines without any technical alterations. The scientist also predicts that hydrogen-powered aircraft could be built to travel at a speed four times of present supersonic air-liners.

[*Indian Engng. News Rec.*, 26 (Nov. 7) (1974), 1]

Synthetic Fuels

Exxon Corporation has decided to expand the current programme of Esso Research and Engineering on coal conversion in USA and at the same time to form a new task force which will plan the development of a commercial coal gasification project using existing technology and based on Exxon coal resources in Wyoming (USA). The latter project may require an expenditure as high as \$400 million.

The research programme of Esso Research & Engineering, started in 1966, will be continued over the next 6 years at an estimated cost of \$8200 million several times the previous expenditure. Construction is shortly to start on two large pilot plants—one, with an input capacity of 500 ton/day for coal gasification by a new process and other for the conversion of coal into synthetic crude oil or alternatively low-sulphur fuel oil.

[*Oil Commentary*, 12 (5) (1974), 22]

Carbon Monoxide Recovery

Kinetic Technology International B.V. [formerly Sales of America (Netherland) NV] has acquired an agreement with Tenneco Chemicals Inc. permitting KTI to design and construct CO-recovery plants throughout the world, according to the latter's new non-corrosive absorption/stripping process named COSORB. This process supplements the conventional processes using cryogenic recovery of CO, thus reducing investment and operating costs by 30%. Carbon monoxide can be recovered from almost any CO-containing streams, such as synthesis gases, methanol plant off-gases, blast furnace top gas, refinery gas, etc. In this cryogenic recovery, the pressure of nitrogen imposes no problem. KTI expects a break-

through towards a CO-based chemical industry providing carbon monoxide as an inexpensive building block.

[*Oil Commentary*, 12 (5) (1974), 23]

China May Rival Middle East in Oil Production

China's oil output is increasing at an annual rate of 30%, to make it likely that China would rival the Middle East as a major oil-producing country in the future, according to Japanese correspondents who recently visited that country. It has now 80 oil-yielding wells located in Manchuria, Shantung and the Tientsin port area and other inland areas of north-east China. Oil exploration is being advanced rapidly in the Pohai Bay and new oil deposits have been discovered recently in Kwantung and Hupeh provinces. Japan's oil import from China this year will amount to 4,500,000 tons which might exceed ten million tons after 3-4 years.

[*Oil Commentary*, 12 (5) (1974), 27]

Industrial Phosphates

Messrs Hindustan Lever Ltd. propose to manufacture industrial phosphates (STPP) from phosphoric acid manufactured by the wet process in their proposed factory at Haldia (W. Bengal). They have invited negotiations for the supply of well-proven and up-to-date technology and know-how.

[*J. Instn. of Chem.* 46 (3) (1974), 101]

Fertilizer Unit in Maharashtra

Maharashtra has decided to sponsor a Rs. 31 crores phosphatic fertilizer project through the Konkan Development Corporation to be located at Apta (Panvel), 60 km from the Nhara-Sheva. The first stage of the project envisage the manufacture of 2.5 lakh tonnes of monoammonium phosphate and about 1.2 lakh tonnes of sulphuric acid. It is intended that ultimately rock phosphate will be received with 80,000 ton capacity ships which will berth only if deep water port Nhara-Sheva is ready.

World Energy Crisis

At the 23rd annual gathering of the Nobel Prize winners held recently in Landau, W. Germany, Prof. Dennis Gabor of London dealt with the fuel and power crisis, which he termed scarcity occasioned by over-indulgence for which the industrialized countries having only themselves to blame. For at least a decade, it had been a well-known fact that unbounden exploitation of natural resources was bound to lead to disaster unless fresh sources of power were discovered. Industrial

civilization and progressive democratization can only be maintained provided 'luxuries' are forgone in research and development and all endeavours are concentrated on locating fresh sources of fuel and power without delay.

According to Isidore I. Rabi, nuclear scientist, international control of nuclear fission on one hand and peaceful exploitation of atomic energy on the other would serve to interlink the peoples of the world. The West must try to forge even closer links with USSR and China in order to further these goals.

Methane from Garbage

Our Indian approach of a cowdung gas plant appears to have its counterparts even in U.S.A. An Indian farmer has installed his version of a gas plant from cow manure and runs his auto engine, gas stove, pumps, space heater, lighting, etc. It appears that this unit was designed on the basis of Indian experience and particulars of U.S. efforts can be had from Mother Earth News, B.A. 70—Hendersonville NC 28739. This news has come in no less prestigious a journal than *Hydrocarbon Processing*, W. M. Inc. of Oak Brook Illinois have also installed a fermentation pilot plant in association with Allis Chalmers. The city wastes are shredded separately magnetically from iron classified with air to get organic light fractions which are mostly waste paper and this fraction is fermented with sewage sludge at 60°C for a period of five days to generate the gas.

While the fermentation approach is the right one for smaller units largely engaged in cattle farming, the approach to city garbage disposal is generally one of pyrolysis or incineration to generate steam. A unit for pyrolysis is being installed by a brewery in Denver which expects to get the fuel from its wastes to the extent of 1 ton coal equivalent for every 2 tons. Pyrolysis to generate liquid fuels is also under development. One party expects methane to come out of garbage used as landfills provided it is deep enough.

While there is some progress on cowdung gas plants in India there is still no systematic plan to stop burning cowdung cake and to maximize the indirect benefits as fuel and manure.

Source: Chemical Industry Development, VIII, 7, 62 (1974)

[*Ind. J. Environ. Hlth.*, 16 (1974), 385]

National Fertilizer Company

A new state fertilizer company, National Fertilizers Ltd., has been

established in India to implement the three inland fertilizer projects, viz. at Bhatinda, Panipat and Mathura, in the Fifth plan. The plants were to be partly financed by Japanese credit. A Rs. 33 crores credit arrangement has been signed with Japan to cover the foreign exchange costs of the Bhatinda project and Toyo Engineering Corp. has been contracted for the engineering services of the plant.

International Fertilizer Fund

The need for swift action on the proposal for an international fertilizers supply scheme made by the UN Commission on Fertilizers in Ceylon in December, 1973 was recognized at a meeting of FAO in Rome in July, 1974. It was agreed that priority should be given to countries which qualify for assistance from UN Emergency operation specially the least developed and land-locked nations. The Director General, FAO, proposed that the scheme's target should be that no developing country should have a lower aggregate supply of fertilizer in 1974-75 than it did in 1973-74 and a 12 per cent growth should be achieved where possible. This would result in an increase in total imports of 1 mil. tons.

The Council authorized the establishment of a fertilizer pool which would receive contributions of cash and fertilizers; the money would be used to purchase fertilizer for countries with balance-of-payments difficulties, to meet shipping costs and to improve the efficiency and output of plants in the developing countries. An important aspect of the fund is the information system, which would provide technical aid to developing countries and an exchange of information on the fertilizer supply and investment needs of the developing countries and the expansion plans of the fertilizer industry. The importance of co-operation with other UN organizations such as World Bank was emphasized. The FAO Council urged that financial assistance be provided for developing countries to build plants to use their indigenous raw materials.

[*Fert. Intert.*, No. 64 (Oct.), 1974, 3]

World Oil Surplus by 1985

After the recent world-wide oil shortage, energy experts now calculate that there will be surplus of oil on the world market again by the end of the decade. The economy measures and technological advances brought in by the oil-consuming countries will have brought actual consumption down to 10 per cent in the industrialized states or 15 per cent in the developing ones below the current estimates. On this basis,

there would be a world surplus of oil supplies over demand of 775 million tonnes as early as 1980 and by 1985 this gap would be as wide as 1000 million.

The experts conclude that oil prices will probably settle down. By 1980 W. Europe will be having oil imports at 1 million barrels a day owing to production from its own sources in the North Sea; 5 years later this figure is likely to double. By 1985, coal production should save W. Europe another 1.2 million barrels a day of imported oil. By the same date, China can be expected to be exporting a further 2-4 million barrels a day, and if USSR manages to exploit its energy reserves in its northern areas, this could also result in additional supplies.

[*Chem. Take-Off*, 4 (1) (1974), 26]

Loan for a Fertilizer Project

The World Bank has extended a loan of \$109 million (approx. Rs. 85 crores) for the co-operative fertilizer project at Phulpur, near Allahabad (U.P.). The loan will finance the construction of the plant which will produce 900 tes/day of urea. The project is scheduled to start commercial production in 1978. The loan will be for 16 years including 5 years of grace with interest at 8 per cent.

Environmental Pollution

A 2-day seminar on environmental pollution due to mining, metallurgical and chemical industries, sponsored by the Mining & Metallurgical Division, Chemical Engineering Division and Dhanbad Sub-centre of the Institution of Engineers, was held in the Indian School of Mines, Dhanbad, on December 21 and 22, 1974. About 70 delegates from different regions of the country attended the seminar and 28 papers were presented and discussed in six technical sessions. Three industry-wise groups were formed for formula of necessary recommendations. One paper by Dr. M. K. Chakraborty and his three co-workers of Central Mining Research Station dealt on air pollution in Dhanbad and its surrounding mining areas. The study covers five aspects of pollution.

[*Coal-field Times*, 28 (39) (1974), 11]

Award

Cheethambadi Aravindakshan Thirumulpad, Assistant Superintendent, Physical Research Wing, P & D Division, FCI Ltd., has been awarded the Ph.D. Degree (1974) by the University of Madras, for his thesis, 'Studies on Fertilizers and Materials Related to Fertilizer Industry', submitted in October, 1971. He carried out this work under the guidance of

Dr. B. K. Banerjee, D.Phil, D.Sc., F.R.I.C., Superintendent and Head of the Physical Research Wing, Planning & Development Division, FCI Ltd.

In one part of the thesis, Dr. C. Aravindakshan has made a thorough investigation on the phase composition and characterization up to the stage of unit cell parameters of 'Urea-from Fertilizers', prepared at different pH and molecular ratios and he has correlated the slow and long nitrification characteristics of the fertilizers to its different constituents. In the other part he has done extensive work on metals, alloys, metal oxides and corrosion. The tempering characteristics of a low alloy of iron has shown an interesting observation that bainitic structures are possible to be produced by continuous cooling and tempering instead of the isothermal cooling. An amalgamation process producing alloys in equilibrium at comparatively low temperatures can have an impact on production of alloys by the powder metallurgy process. The work on metal oxides has shown the existence of three new nickel oxide hydrates and the evidence of tetrahedral coordination to nickel. A few more modifications for niobium pentoxide have been shown to exist; and the reasons for various modifications have been resolved as due to niobium atoms occupying one of the several possible positions of tetrahedral or octahedral sites of the block structure. In addition to the above, his long investigations on corrosion has revealed that many immature carbon and alloy steel corrosion failures in fertilizer process environments were mainly due to additive action of impurities and fabrication defects which were hitherto thought to be negligible from corrosion point of view. In all cases, the mechanism of corrosion has also been determined.

Besides, Dr. C. Aravindakshan has made many significant contributions in the field of crystal structure, metal physics and corrosion, which were published in the leading journals of India and abroad. He was also elected as a Member of Indian Institute of Metals (India) in 1973.

Patents*

Benefication and Briquetting of Phosphate Ores. R. I. Howard and J. K. Sullivan (to FMC Corp.). U.S. 3,773,473, Nov. 20, 1973, Appl. Oct. 2, 1969; 6 pp. A beneficiated, calcined phosphate agglomerate, useful as a P furnace feed, is produced. Phosphate shale is crushed to $\frac{1}{4}$ to $\frac{1}{8}$ in. particles and calcined in a fluidized bed at 1500-2200°F. A P-poor, -400 mesh fraction is removed without recycle, overhead from a relatively P-rich fraction remaining in the fluidized bed. The P-rich fraction is withdrawn and briquetted under sufficiently high pressure and temperature to cause plastic flow of the ore and produce the calcined phosphate agglomerate.

[Fertilizer Abstracts, 6 (1974), 132]

Briquetting and Calcining Western Phosphate Shale Ore. J. K. Sullivan and R. I. Howard (to FMC Corp.). U.S. 3,760,048 Sept., 18, 1973, Appl. Apr. 22, 1970; 9 pp. A method is described for producing a strong, calcined phosphate agglomerate, useful as a P furnace feed, from mine run western phosphate shale ore. The ore is crushed to substantially $\frac{1}{4}$ to $\frac{1}{8}$ in. and agglomerated with sufficient H₂O to produce agglomerates containing 9-12, preferably 10-11.5% moisture. By means of a non-agitated perforate grate, the bed of agglomerates is conveyed through a calcining zone at 2000-2500°F for 15-25 min. The calcined agglomerates are cooled and recovered from the nonagitated grate.

[Fertilizer Abstracts, 6 (1974), 132]

Nitrogen-Phosphorus Compounds. H. T. Lewis, Jr. and J. G. Getsinger (to Tennessee Valley Authority). U.S. Patent Office Defensive Publication T 921, 003, Apr. 2, 1974, Appl. Mar. 16, 1973; 30 pp. A vapor phase reaction process is described for production of concentrated N-P compositions. Elemental P is simultaneously reacted with a low proportion of input NH₃ and an excess of O₂ (air) in a single stage reactor. Input O₂ (air) ranges from ~120-800 wt % most preferably 375%, of that required to yield an O₂:P₄ mole ratio of 5. The quantity of input NH₃

* These patents have been reproduced from *Fertilizer Abstracts* published by the National Fertilizer Development Centre, TVA, Muscle Shoals, Alabama (USA), with kind permission of Editor, FA.

—Editor.

ranges from ~50-80 wt % of that required to yield a N:P atomic ratio of 2. The reactor (tube) is maintained at ~500—1300°F and has a maximum surface area: volume ratio of ~0.8 in.²/in.³. Retention time of gases in the reactor ranges from ~0.5-3.5 sec at operating conditions, but 1 sec is most preferred. The product of the reaction gases is collected as dry, white, amorphous solid containing N 14-16, P 31-33, and total plant nutrient up to 91 wt % (N+P₂O₅ equivalent). Water solubility of the solid products ranges from ~90-100 wt %. Greenhouse tests indicate that the products are fully effective as fertilizer.

[Fertilizer Abstracts, 6 (1974), 134]

Agent and Method for Determination of Calcium. Roland Helger (to Merck Patent G.m.b.H.). U.S. 3,798,000, Mar. 19, 1974, Appl. Ger. Sept. 3, 1971; 4 pp. The colorimetric determination of Ca²⁺ is carried out using a Ca²⁺ complexing color reagent, for example a mixture of phthalein purple and 8-hydroxyquinoline sulfate, together with a buffer consisting of amidosulfonic acid, Na₂B₄O₇ and Na₂CO₃ or K₂CO₃. The buffer is used as an aqueous solution; the color reagent and the amidosulfonic acid are pressed into tablets. In an example, the aqueous buffer solution contained 45.3 × 10⁻³ mole/l. of Na₂B₄O₇ · 10H₂O and 0.1 mole/l. of Na₂CO₃. The tableted color reagent contained phthalein purple 0.60, 8-hydroxyquinoline sulfate 11.20, amidosulfonic acid 43.98, and lactose binder 42.22 mg.

[Fertilizer Abstracts, 6 (1974), 137]

Prilled Ammonium Nitrate Having Improved Anticaking and Antidusting Properties. Konoshuke Fujiki *et al* (to Mitsubishi Chemical Industries, Ltd.). U.S. 3,779,821, Dec. 18, 1973, Appl. Japan Sept. 27, 1971; 6 pp. The title product is produced by blending NH₄NO₃ prills with 0.05-1.0 wt % of a petroleum hydrocarbon of boiling point > 150° and melting point < 20° and 0.01—0.5 wt % of an anticaking agent. Suitable hydrocarbons include processing oils such as cutting oil and quenching oil; light lubrication oils such as spindle oil, refrigerating oil, and turbine oil; and mixtures thereof. The anticaking oil, and turbine oil; and mixtures thereof. The anticaking agent may be selected, from Al-, Ba-, Ca-, Cd-, Cu-, Mg-, Pb- and Zn-steates; Mg caprate; and Mg undecanate. Petroleum hydrocarbon may be added first followed by the anticaking

agent, or the two materials may be added simultaneously.

[Fertilizer Abstracts, 7 (1974), 157]

Fixation of Nitrogen by Irradiation to Form Nitrates. E. R. Johnson and E. W. Holtzheiter, Jr., (to United States of America as represented by the United States Atomic Energy Commission). U.S. 3,801,484, Apr. 2, 1974, Appl. Oct. 13, 1972; 1 p. A method is described for making a nitrate or nitrite by contacting a N-O mixture such as air with an alkali metal perbromate, bromate, bromite, or hypobromite in the presence of ionizing gamma radiation. Typically, the alkali metal Br-containing compound is KBrO_3 . In an example, a 1 g mass of 100 mesh KBrO_3 was irradiated with a ^{60}Co source in the presence of air at 25° and 1 atm to a dose of 5×10^{23} electron volts/g. The reaction products contained KNO_3 15 and KNO_2 4 mole % as well as bromides, Br_2 , and oxybromides. The method is especially useful for small-scale production of nitrates and nitrites enriched in specific isotopes of either O_2 or N_2 or both.

[Fertilizer Abstracts, 7 (1974), 157]

Wet-Process Phosphoric Acid from Underground Phosphate Rock. D. R. Randolph and R. L. Bristow (to American Cyanamid Co.). U.S. 3,803,293, Apr. 9, 1974, Appl. May 26, 1972; 8 pp. Underground phosphate rock of surface area 10-50 cm^2/g typically containing 3-7 wt % moisture and having 65-79 wt % of -4+35 mesh material is slurried under agitation at 75-84° with recycled H_3PO_4 from the process containing < 1.5 wt % free H_2SO_4 . While maintaining the temperature and the free H_2SO_4 levels constant, additional H_2SO_4 is added to dissolve ~ 90 wt % of the rock particles, which are kept in suspension by agitation. The H_3PO_4 is separated from the resulting H_3PO_4 - CaHPO_4 - CaSO_4 slurry and recovered as product. Liquid-solid slurry remaining from the separation is admixed with sufficient H_2SO_4 to increase the free H_2SO_4 content to 5-20 wt % and heated to 85-90° under agitation until the CaHPO_4 content is < ~ 0.9 wt %. The resulting H_2SO_4 - H_3PO_4 mixture is separated from the slurry and recycled to the process for admixture with the phosphate rock in the first reaction stage. In an example, overall recovery of P_2O_5 in the process was 98.25-99.2%.

[Fertilizer Abstracts, 7 (1974), 159]

Plaster from Phosphogypsum G. H. Vincent (to Combustion Engineering, Inc.) U.S. 3,782,986, Jan. 1, 1974, Appl. Nov. 12, 1970; 2 pp. Phosphogypsum dried to ≤ 1.0 wt % free H_2O is milled to a Blaine surface area of $\geq 4000 \text{ cm}^2/\text{g}$, mixed with 0.25-1.0 wt % of dry H_3BO_3 , and calcined to produce plaster. About 0.25-5.0 wt % of $\text{Mg}(\text{OH})_2$ is then added to the dry plaster and the mixture is milled to a Blaine surface area of $\geq 9000 \text{ cm}^2/\text{g}$. Alternately, the $\text{Mg}(\text{OH})_2$ may be added during the calcination step. The H_3BO_3 acts as a calcination modifier, produces a plaster particle of increased surface area, and decreases the setting time. Addition of the $\text{Mg}(\text{OH})_2$ produces a significant increase in the compressive strength of the plaster, for example from ~1600 to ~2200 lbs./in^2 .

[Fertilizer Abstracts, 7 (1974), 159]

Addition of Zinc Compositions to Liquid Fertilizers R. J. Windgassen (to Standard Oil Company). U.S. 3,796,559, Mar. 12, 1974, Appl. Jan. 8, 1973; 4 pp. Normally when Zn particulate compositions are added to a base liquid fertilizer, lumping and caking of the Zn material occurs. This lumping and caking is prevented by coating the particulate Zn compositions with an alkyl phosphine containing 6-40 C atoms before adding the Zn material to the base liquid fertilizer.

[Fertilizer Abstracts, 7 (1974), 159]

Hydrated Octa Calcium Phosphate. R. H. Carlson (to Hooker Chemical Corp.). U.S. 3,764,656 Oct. 9, 1973, App. Feb. 25, 1972; 3 pp. The P values solutions, such as phosphate crystal mother liquor containing primary, secondary, or tri-alkali metal or ammonium phosphates, are recovered as hydrated octa Ca phosphate by treatment of the solutions with a slurry of CaSO_4 at Ca:P mole ratio of 1.30-1.35:1, pH 4-6, and 80-90°C. Phosphate recovery ranges from ~ 80 > 93%. The product typically contains PO_4 7-50.5, SO_4 3.0-6.0, Ca 30.0-32.5, and F_2O_4 0-0.6%. The Ca:P mole ratio is 1.26-1.36:1 and the P:F wt. ratio is 26-41:1.

[Fertilizer Abstracts, 7 (1974), 160]

Nitrogen-Phosphorus Compounds Containing Amido Phosphates. B. G. Bennett and W. S. Holmes (to Albright and Wilson, Ltd.) U.S. 3,788,986, Jan 29, 1974 Appl. Sept. 13, 1972; 2 pp. The title com-

pounds are prepared at superatmospheric pressure in a two-stage process from liquid NH_3 at -33° and solid P_2O_5 . A dispersion of P_2O_5 in liquid NH_3 is formed by adding the solid P_2O_5 liquid NH_3 at an $\text{NH}_3:\text{P}_2\text{O}_5$ wt ratio of -3:1 with mixing to prevent local temperatures from exceeding 100°. The reaction mixture is then maintained at 70-80° in the presence of a catalytic amount of H_2O until the desired degree of reaction is achieved. A typical product of N:P rate -2.45+1 contained $\text{PO}(\text{NH}_2)_3$ 10.7, $\text{NH}_2\text{PO}_2-(\text{NH}_2)_2$ 37.4, NH_4HPO_3 $(\text{NH}_2)-7.3$, $(\text{NH}_4)_2\text{HPO}_4$ 2.4, and higher phosphates 42.2%. Alternatively, the products may be heated to -100° to form condensed materials suitable as flame retardents.

[Fertilizer Abstracts, 7 (1974), 161]

Removal of Nitric Oxides from Nitric Acid Plant Tail Gases. Georg von Semel and Eduard Schibilla (to Friedrich Uhde G.m.b.H.). U.S. 3,809,744, May 7, 1974, Appl. Ger. Apr. 6, 1971; 3 pp. The concentration of NO in tail gases from HNO_3 plants is reduced by scrubbing the gases at 1-7 atm with a nitric vanadium solution containing preferably 2.0-3.0% V_2O_5 and 10-30% HNO_3 . Effluent solution is regenerated by heating the solution to a temperature ranging from 90° to the boiling point and stripping with air. The regenerated vanadium solution is reused as scrubbing fluid and the concentrated NO_2 gas removed can be sent to the absorption towers of the HNO_3 plant. In an example, absorption of nitric oxides by the scrubbing solution was as high as 91.7%.

[Fertilizer Abstracts, 8 (1974), 183]

Ammonia and Hydrogen Chloride from Ammonium Chloride Scott Lynn and R. C. Forrester III (to the Regents, Univ. California). U.S. 3,792,153 Feb. 12, 1974, Appl. Feb. 28, 1972; 4 pp. Aqueous solutions of NH_4Cl are causticized with reactive MgO to yield NH_3 , $\text{Mg}(\text{Cl})_2$, and H_2O . After separating the NH_3 , the aqueous $\text{Mg}(\text{Cl})_2$ is thermally decomposed at $> 700^\circ$ in the presence of H_2O to yield HCl and reactive MgO . The HCl is removed and the reactive MgO is recycled to the causticizing step to react with additional $(\text{NH}_3)_4\text{Cl}$. Alternately, basic MgCl_2 may be substituted for the reactive MgO in the process.

[Fertilizer Abstracts, 8 (1974), 183]

Solid Polyphosphoric Acid P. J. Melver (to Comminco, Ltd.). U.S. 3,777,008 Dec., 4, 1973, Appl. Canada Sept. 24, 1969; 7 pp. Solid polyphosphoric acid of $\geq 98\%$ H_2O solubility is prepared from wet-process H_3PO_4 containing at least one of the cationic materials Al, Fe, Mg, Ca, K, Cu, Mn, Mo, Zn, Co, Na, and NH_4 — at a metallic element : P_2O_5 mole ratio of 0.18-1.05. The wet-process

H_3PO_4 is passed through an electrothermal cell where a controlled ac potential is applied to concentrate the acid at $335-600^\circ$ to $\sim 82\%$ P_2O_5 . Sufficient flow of acid is maintained to prevent formation of insoluble material. Solid polyphosphoric acid is obtained by cooling the concentrated acid leaving the electrothermal cell. Supplemental cationic materials in the form of plant nutrient elements

may be added to the feed acid. A prilled polyphosphoric acid product may be obtained by cooling the concentrated acid discharging from the electrothermal cell in a liquid prilling medium consisting of the ammoniated low molecular wt hydrocarbon chloroform, trichloroethylene, perchloroethylene, or mixtures thereof.

(Fertilizer Abstracts, 8 (1974), 185)

PUBLICATIONS OF FERTILIZER CORPORATION OF INDIA AVAILABLE FOR SALE

1. **Proceedings of the Seminar on Wastes & Effluents in Chemical Industries, Sindri, May 2-3, 1965** (103 pages) Price: Rs. 7.00 (by ordinary post; registered parcel/V.P.P. charges extra) and no discount. Contains 29 papers by distinguished scientists and technologists on the problem of industrial wastes and effluents, and measures to check pollution.
2. **Proceedings of the Seminar on Coal and Coal Chemicals Sindri, November 2-3, 1968** (184 pages). Price: Rs. 18.50 (by ordinary post; registered parcel/V.P.P. charges extra). Contains 31 papers by eminent scientists and also the First Dr. H. L. Roy Memorial Lecture.
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STATISTICS

TABLE 1—COST MATRIX FOR NITROGEN: 1973-74 (Kharif)

(Unit Cost in Rupees)

State Factory	Assam 1	W.B. 2	Bihar 3	Orissa 4	A.P. 5	T.N. 6	Kerala 7	Mysore 8	Mah 9	Guj. 10	MP. 11	Raj 12	U.P. 13	MR. 14	Pb. 15	H.P. 16	J & K 17	Production (Te.)
1. FCI Namrup	127	275	278	345	423	475	477	477	452	455	380	420	375	409	320	450	450	18000
2. HSL Durgapur	242	47	82	147	335	471	481	478	429	438	266	349	227	331	362	409	409	1748
3. FCI Durgapur	126	23	45	76	175	245	250	249	223	228	138	182	118	172	188	213	213	41800
4. FCI Sindri	207	155	95	112	290	426	433	433	389	292	235	298	187	267	319	365	365	36000
5. HSL Rourkela	224	102	132	146	220	348	353	353	312	330	172	330	195	298	334	366	366	50308
6. Coromendal Vizag	223	133	141	78	65	163	168	168	158	225	133	227	168	215	235	255	255	32000
7. Neyveli lignite, Neyveli	282	238	255	202	113	37	77	96	172	233	230	257	259	266	281	288	288	2800
8. Madras Fert. Manali	288	250	264	216	141	35	78	118	188	245	244	264	266	275	285	294	294	65600
9. FACT Ltd., Alwaye	553	484	506	418	276	142	56	227	357	468	471	515	510	528	548	564	564	32800
10. FCI Trombay	497	416	395	410	278	371	380	255	102	154	250	255	325	338	376	413	413	32400
11. G.S.F.C. Baroda	330	286	261	299	238	290	293	223	125	39	159	117	195	152	178	212	212	86400
12. Shriram Chem. Kota	245	184	163	202	191	255	259	232	146	88	94	67	98	86	112	141	141	44000
13. FCI Gorakhpur	163	92	64	144	220	273	275	261	200	186	128	136	55	131	136	163	163	32000
14. Indian Explo- sive Kanpur	200	123	97	170	191	257	259	240	168	154	88	97	25	101	108	149	149	80000
15. FCI Nangal	394	309	276	369	375	447	449	431	350	248	269	164	176	92	87	130	137	32000

TABLE 2—COST MATRIX FOR P₂O₅: 1973-74 (Kharif)

State Factory	Assam 1	W.B. 2	Bihar 3	Orissa 4	A.P. 5	T.N. 6	Kerala 7	Mysore 8	Mah 9	Guj. 10	MP. 11	Raj 12	U.P. 13	MR. 14	Pb. 15	H.P. 16	J & K 17	Production (Te.)
1. Bihar State Super, Sindri	281	74	328	165	393	577	586	586	526	531	318	404	253	375	432	494	494	1504
2. Coromendal Fert. Lt., Vizag	366	219	231	129	160	268	276	275	260	369	219	372	276	352	386	418	418	29200
3. E.I.D. Perry Ltd., Ranipat	668	535	577	426	217	165	203	194	349	522	516	581	589	619	657	691	691	6680
4. Shaw Wallace & Co. Avadi	651	511	552	398	189	168	203	179	318	494	488	560	569	598	646	674	674	4872
5. Madras Fert. Ltd., Manali	663	576	607	498	324	80	180	271	433	565	561	606	611	631	656	676	676	3400
6. FACT Ltd., Alwaye	663	622	607	498	331	169	66	271	428	561	561	617	611	633	656	676	676	16580
7. Mysore Chem. & Fer. Belagula	702	594	629	505	311	234	275	112	362	505	522	589	646	623	663	691	691	2144
8. FCI Trombay	622	521	494	513	348	465	475	319	128	193	313	319	407	423	470	517	517	14400
9. Dharmasi Morarji, Amber Nath	567	467	439	467	310	411	425	383	105	185	294	294	378	387	435	475	475	9544
10. GSFC, Baroda	261	227	207	237	188	230	232	277	98	30	126	93	149	120	141	168	168	20736
11. Alembic Chem. Works, Baroda	646	560	511	586	466	569	573	438	243	77	311	231	368	299	349	415	415	1504
12. Dharmasi Morarji, Bhilai	499	324	305	293	201	516	526	494	343	381	171	409	293	415	460	526	522	4800
13. D.C.M. Chem. Delhi	543	421	324	531	516	675	663	623	460	305	318	168	228	64	150	228	228	8448

[Industr. Engng. & Management, 9 (2) (1974), 36 & 37]

TABLE 3—INSTALLED GENERATING CAPACITY AND
POWER PRODUCTION IN INDIA

Year	Installed Capacity, million kW	Total Energy Generation, million kWh	kWh/kW Installed
1947	1.9	4935	2740
1950-51	2.3	6574	3000
1955-56	3.42	10777	3260
1960-61	5.66	20123	3840
1965-66	10.17	36825	3960
1970-71	17.00	65214	4000

Source : Oil Commentary, New Delhi 1973.

[*Indian & Foreign Review*, (Aug. 1, 1974), 20]

TABLE 4—ENERGY CONSUMPTION IN MILLION TONNES OF COAL EQUIVALENT IN INDIA

Period	Commercial Energy						Non-commercial Energy				Grand Total
	Coal	Lignite	Oil	Hydro	Nuclear	Total	Dung	Fire Wood	Vegetable Waste	Total	
1968-69	69.50	2.25	84.30	15.20	—	171.25	19.70	135.10	32.6	187.40	358.65
1974-74	93.50	4.00	152.60	22.63	4.23	276.96	22.60	155.10	35.1	212.80	489.70
1978-79	130.00	6.35	214.00	35.00	10.15	394.50	24.90	170.50	38.0	233.40	627.90
1980-81	145.00	6.66	253.00	43.50	12.60	460.76	25.86	178.22	39.2	243.28	704.64
1983-84	178.00	8.65	329.00	62.40	20.00	598.26	25.50	175.00	39.5	240.00	836.50
1984-85	200.00	10.00	380.00	75.00	25.00	690.00	25.00	170.00	40.0	235.00	925.00

Source : Associated Chambers of Commerce and Industry, Calcutta, 1974

[*Indian & Foreign Review*, (Aug 1, 1974), 19]

TABLE 5—INVESTMENT IN POWER SUPPLY INDUSTRY IN INDIA

Period	Rs. (in Million)
Pre-Plan Period	1900
First Plan	3020
Second Plan	5250
Third Plan	13810
Annual Plans (1966-69)	12530
Fourth Plan (Estimates)	25230
Fifth Plan (Proposed)	33230

Source : Planning Commission, New Delhi.

[*Indian & Foreign Review*, (Aug. 1, 1974), 21]

TABLE 6—PRODUCTION, HOME DELIVERIES AND TRADE OF PHOSPHATE ROCK, (mil. tes)

Region	Production		Home Deliveries		Exports		Imports	
	1972	1973	1972	1973	1972	1973	1972	1973
West Europe of which EEC	0.1	0.1	0.1	0.1	—	—	20.4	22.4
East Europe	0.1	0.1	0.1	0.1	—	—	15.7	17.1
North America	19.7	27.3	13.4	15.1	6.3	6.2	8.4	8.4
Latin America	36.9	37.6	26.6	28.3	12.5	12.3	2.7	3.1
Africa	0.4	0.5	0.3	0.4	0.1	0.1	2.3	2.5
Asia	23.7	27.4	3.9	4.2	19.9	23.4	—	0.2
Oceania	5.1	5.9	3.4	3.9	1.8	2.0	7.0	7.7
Total Western World	3.0	4.6	—	—	2.9	4.6	2.7	4.3
Total Eastern Block	66.0	72.3	31.3	33.3	37.0	42.2	33.9	38.5
World Total	22.9	25.1	16.4	18.7	6.5	6.4	9.6	9.9
	88.9	97.4	47.7	52.0	43.5	48.6*	43.5	48.4*

* Total differ due to incomplete breakdown of exports by destination.

[*Industrial Minerals*, 80 (May, 1974), 36]

TABLE 7—FORECAST WORLD POTASH CONSUMPTION UPTO 1980
(Million S. Tons K₂O)

	1971	1975	1980
North America	5.1	6.0	7.3
Central and South Africa	0.9	1.3	2.0
Asia	1.6	2.2	3.2
Africa	0.3	0.4	0.7
Western Europe	5.1	5.7	6.7
Eastern Europe	5.7	7.3	10.1
Oceania	0.2	0.4	0.7
Total	18.9	23.3	30.6

Source : Canadian Department of Mineral Resources

[*Industrial Minerals*, 80 (May 1974), 19]

